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the value  $D_4^{20}$  0.7912. Thus the range of published figures varies from 0.79072 to 0.79197 for the density of acetone at  $20^\circ/4^\circ$ . The result obtained in the present work is the mean of two which agreed exactly, namely, 0.79082. The specific gravities in this work are given to five decimal places, by which is meant that they are correct to four places, the fifth figure being doubtful in each case. It will be seen, therefore, that excellent agreement is obtained with the result of Squibb ( $D_4^{20}$  0.7908) and with that of Perkin ( $D_4^{20}$  0.79072).

The results for the density of acetone at other temperatures agree well with those obtained by Bramley (*loc. cit.*), as shown in the following table.

TABLE V.

*Comparison of Results for Density of Acetone at Various Temperatures.*

| Temperature.       | Density. |          |
|--------------------|----------|----------|
|                    | Author.  | Bramley. |
| $20^\circ/4^\circ$ | 0.79082  | 0.7912   |
| $30^\circ/4^\circ$ | 0.77931  | 0.7793   |
| $40^\circ/4^\circ$ | 0.76784  | 0.7674   |
| $50^\circ/4^\circ$ | 0.75599  | 0.7555   |

The density of methyl ethyl ketone is given by Marshall (T., 1906, **89**, 1376) as 0.81005 at  $15^\circ/4^\circ$ . Extrapolation from the results obtained by the present author gives 0.8101, which agrees very well with Marshall's figure.

The density-concentration curves are all straight lines parallel to each other, thus showing that there is no contraction or expansion in volume on mixing acetone and methyl ethyl ketone at any of the temperatures  $20^\circ$  to  $50^\circ$ .

The density-temperature curves for the pure liquids and for the mixtures are also practically straight lines, the curvature being extremely slight. For acetone, the difference in density per degree over the whole range is 0.001161, and for methyl ethyl ketone it is 0.00106.

#### Summary.

Vapour pressures and densities of acetone, methyl ethyl ketone, and mixtures of the two have been determined from  $20^\circ$  to  $50^\circ$ .

The vapour pressure-concentration curves all lie between the vapour pressures of the components, there being no sign of a maximum at any point.

The density-concentration curves are straight lines, showing that

no change in volume occurs when acetone and methyl ethyl ketone are mixed in any proportions from 20° to 50°.

In conclusion, the author's best thanks are due to Messrs. Nobel's Explosives Co., Ltd., for whom the work was carried out, and to Mr. Wm. Rintoul, the Manager of the Research Section, for permission to publish the results.

THE RESEARCH LABORATORIES,  
ARDEER.

[Received, July 14th, 1919.]

### XCIX.—*The Constitution of Internal Diazo-oxides (Diazophenols). Part II.*

By GILBERT T. MORGAN and ERIC DODDRELL EVENS.

EARLIER experiments on the nitrated ortho- and para-diazo-oxides of the benzene series showed that 4-nitrobenzene-1-diazo-2-oxide obtained by the diazotisation of 5-nitro-2-aminophenol has the property of forming dihydroxyazo-derivatives which yield metallic lakes having remarkably distinctive colours (Morgan and Porter, T., 1915, 107, 645).

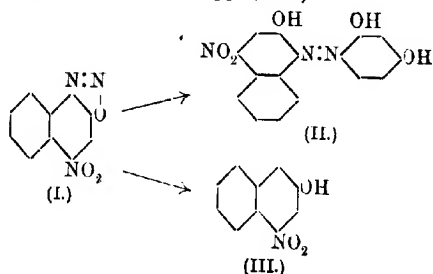
In the present investigation the corresponding diazo-oxide of naphthalene has been examined from this point of view. The results afford an interesting comparison of the differences manifested between benzenoid diazo-oxides and their analogues in the naphthalene series.

4-Nitronaphthalene-1-diazo-2-oxide (I) was first obtained by Friedländer, who passed nitrous fumes into a solution of 2:4-dinitro- $\alpha$ -naphthylamine in moderately concentrated sulphuric acid and added the diazo-solution to alcohol or water (*Ber.*, 1895, 28, 1951).

The product, which can be prepared in quantitative yield by the methods described in the present paper, has not hitherto been examined in any detail. This very stable internal diazo-oxide couples only with the more reactive phenols, such as resorcinol, phloroglucinol, and 1:3-dihydroxynaphthalene, and in these instances the formation of azo-compounds takes place not only in alkaline solutions but also, and with greater facility, in the presence of strong acids, for example, in glacial acetic acid containing concentrated mineral acid.

4-Nitro- $\beta$ -naphthol-1-azoresorcinol (II) functions as an acid mordant dye giving reddish-brown shades on wool which are changed

into lakes of characteristic colour by the action of metallic mordants (chromium, vanadium, copper, etc.):



On prolonged boiling with ethyl alcohol either alone or in the presence of a metallic catalyst, 4-nitronaphthalene-1-diazo-2-oxide loses its diazo-group and becomes converted into 4-nitro- $\beta$ -naphthol (III), the fourth isomeride to be discovered of the seven possible nitro- $\beta$ -naphthols.

4-Nitro- $\beta$ -naphthol is less reactive than  $\beta$ -naphthol. It is much less easily alkylated, and couples more slowly with azo-compounds. The 4-nitro-1-azo- $\beta$ -naphthols, from benzenediazonium chloride and *p*-nitrobenzenediazonium chloride, are insoluble in aqueous alkali hydroxides, in this respect resembling the azo- $\beta$ -naphthols, the insolubility of which in aqueous alkalis is a matter of so much theoretical interest and industrial importance. The azo-dyes obtained from 4-nitro- $\beta$ -naphthol differ considerably in colour from those derived from  $\beta$ -naphthol.

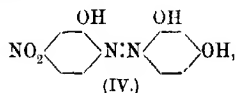
The diazotisation of 2:4-dinitroaniline in concentrated sulphuric acid has already been effected, and the results indicate that the nitro-group is less readily removed than in the foregoing case of 2:4-dinitronaphthalene-1-diazonium sulphate. The elimination of a nitro-group from 2:4-dinitrobenzene-1-diazonium sulphate is not effected merely by dilution with water. In this instance it is necessary to neutralise the solution with alkali carbonate (Badische Anilin- & Soda-Fabrik, D.R.-P., 144640), when a soluble form of 5-nitro-2-diazophenol is produced. Repetition of this experiment showed that the formation of this ortho-diazophenol is not quantitative. An insoluble product is obtained, the amount of which varies from 14 to 20 per cent. of the 2:4-dinitroaniline employed. This by-product, which is still under examination, is an ill-defined substance having the properties of an external diazo-oxide. It couples readily with either alkaline  $\beta$ -naphthol or  $\beta$ -naphthylamine in acetic acid solution.

The soluble variety of 5-nitro-2-diazophenol contained in the

clear, yellow filtrate from the foregoing insoluble product couples with aromatic *m*-diamines, phenols, naphthols, aminonaphthols, and their sulphonic acids.

The azo- $\beta$ -naphthol thus obtained is identical with the compound produced from the insoluble 4-nitrobenzene-1-diazo-2-oxide (M. and P., T., *loc. cit.*).

5-Nitrophenol-2-azoresorcinol (IV),



gives intensely coloured lakes on wool mordanted with metallic hydroxides. Similar dihydroxyazo-dyes are obtained from chromotropic acid and from aminonaphtholsulphonic acids coupled in alkaline solution. These colouring matters are extremely sensitive to metals, and are converted into green, purple, and blue lakes by the action of metallic mordants.

#### Summary.

1. 2:4-Dinitronaphthalene-1-diazonium sulphate is unstable in dilute acid and passes quantitatively into the sparingly soluble 4-nitronaphthalene-1-diazo-2-oxide, a very stable diazo-oxide yielding azo-derivatives only with difficulty.

2. 4-Nitronaphthalene-1-diazo-2-oxide undergoes loss of the diazo-group with the production of 4-nitro- $\beta$ -naphthol.

3. 2:4-Dinitrobenzene-1-diazonium sulphate is stable in dilute acid, but in neutral or slightly alkaline solution it yields the soluble 5-nitro-2-diazophenol together with an insoluble by-product. This soluble diazo-compound furnishes *o*-dihydroxyazo- and *o*-amino-hydroxyazo-dyes, giving intensely coloured lakes with metallic mordants.

#### EXPERIMENTAL.

##### *I. Diazotisation of 2:4-Dinitro- $\alpha$ -naphthylamine Sulphate.*

2:4-Dinitro- $\alpha$ -naphthylamine, the starting point of this part of the investigation, was obtained in three different ways.

1. *Preparation from 2:4-Dinitro- $\alpha$ -naphthol.*—Finely powdered  $\alpha$ -naphthol (50 grams) was added to 100 c.c. of concentrated sulphuric acid and the mixture stirred until a clear solution was obtained. On heating this liquid on the water-bath for fifteen minutes,  $\alpha$ -naphtholdisulphonic acid separated when the mixture

was cooled, and the solidified mass was dissolved in 250 c.c. of water. The cooled solution was added slowly to 60 c.c. of nitric acid (D 1.42), the temperature being maintained below 10°. The nitration mixture was then slowly warmed to 100° and maintained at this temperature for fifteen minutes, the pasty mass being stirred continuously. After cooling, the pale yellow 2:4-dinitro- $\alpha$ -naphthol was collected (m. p. 132°; yield, 83 per cent.).

The authors are indebted to Dr. L. G. Paul for this process, in which the nitration is much more under control than when the nitric acid is added to solutions of  $\alpha$ -naphtholdisulphonic acid. Prolonged sulphonation on the water-bath led to  $\alpha$ -naphtholtrisulphonic acid with subsequent formation of naphthol yellow S.

Dinitro- $\alpha$ -naphthol (60 grams) and 700 c.c. of alcoholic ammonia saturated at 0° were heated for ten hours at 195–200° in a rotating steel autoclave, the pressure attained being 39 kilos. per square cm. 2:4-Dinitro- $\alpha$ -naphthylamine (40 grams) separated from the alcoholic solution on cooling; the filtrate contained the ammonium salt of 2:4-dinitro- $\alpha$ -naphthol together with tarry impurities. When crystallised from glacial acetic acid, 2:4-dinitro- $\alpha$ -naphthylamine melted at 239°. Concentrated aqueous ammonia, under the foregoing conditions, did not affect dinitro- $\alpha$ -naphthol.

2. *Preparation from Aceto- $\alpha$ -naphthalide* (compare Meldola, *Ber.*, 1886, 19, 2683).—Aceto- $\alpha$ -naphthalide (100 grams) was dissolved in 200 c.c. of glacial acetic acid and nitrated with 52 c.c. of nitric acid (D 1.52) mixed with an equal volume of glacial acetic acid. During the addition of the mixed acids, the temperature was kept below 70° and subsequently raised to 96° until the dinitro-compound began to separate. The mixture was then cooled and the separating solid crystallised from glacial acetic acid (yield, 52 per cent.). Twenty grams of purified 2:4-dinitroaceto- $\alpha$ -naphthalide were added to a cold mixture of 30 c.c. of water and 200 c.c. of concentrated sulphuric acid. The mixture was warmed at 60–70° for a few minutes, allowed to cool for fifteen minutes, and poured into 400 c.c. of ice-water, when 2:4-dinitro- $\alpha$ -naphthylamine was precipitated.

3. *Preparation from Toluene-*p*-sulphon- $\alpha$ -naphthylamide*.—Toluene-*p*-sulphon- $\alpha$ -naphthylamide, prepared by trituration together  $\alpha$ -naphthylamine, toluene-*p*-sulphonyl chloride, and anhydrous sodium acetate in molecular proportions, was washed with warm water rendered alkaline with sodium carbonate and crystallised from alcohol (yield, 96 per cent.). Fifty grams of this preparation were dissolved in 400 c.c. of hot glacial acetic acid. The solution when cooled to 45° deposited crystals of the dissolved substance, and the mixture was nitrated with 30 c.c. of nitric acid

(D 1·42) mixed with 30 c.c. of glacial acetic acid. The temperature rose to 60° and the mixture was subsequently heated to 80° for one hour. On cooling, *toluene-p-sulphon-2:4-dinitro- $\alpha$ -naphthylamide* crystallised, and a further crop was obtained on diluting with water. When crystallised from alcohol this compound separated in radiating clusters of pale yellow, silky needles melting at 165—166° (yield, 80 per cent.):

0·3614 gave 36·3 c.c.  $N_2$  at 22° and 763·6 mm.  $N=11·42$ .

$C_{17}H_{13}O_6N_3S$  requires  $N=10·85$  per cent.

This dinitro-compound was hydrolysed by adding 20 grams to a cooled mixture of 200 c.c. of concentrated sulphuric acid and 30 c.c. of water, and warming at 70° for ten minutes. On adding the cooled mixture to ice-cold water, 2:4-dinitro- $\alpha$ -naphthylamine was precipitated, the yield being quantitative.

#### *4-Nitronaphthalene-1-diazo-2-oxide (I).*

2:4-Dinitro- $\alpha$ -naphthylamine (3 grams) was dissolved in 30 c.c. of cold concentrated sulphuric acid, 5·5 grams of nitrosyl sulphate were added, and the solution was diluted with fragments of ice until on further dilution of a portion with water a clear solution was obtained. The main solution of diazotised amine was then poured into 800 c.c. of water and left for one hour, when the precipitated diazo-oxide was collected and crystallised from light petroleum (b. p. 60—80°). This product, which separated in yellow needles, decomposed with intumescence at 130—134°.

The foregoing diazotisation was also effected with dry sodium nitrite dissolved in concentrated sulphuric acid at temperatures below 70°, the solution being cooled before use. Moreover, the diazo-oxide was prepared from the acyl derivatives of 2:4-dinitro- $\alpha$ -naphthylamine without isolating the base itself.

2:4-Dinitroaceto- $\alpha$ -naphthalide (30 grams) or the corresponding amount of *toluene-p-sulphon-2:4-dinitro- $\alpha$ -naphthylamide* added to 300 c.c. of concentrated sulphuric acid diluted with 42 c.c. of water underwent hydrolysis on warming to 70°. After cooling to 0° the solution was treated with 10 grams of sodium nitrite dissolved in 30 c.c. of concentrated sulphuric acid. Fragments of ice were added until a test portion on further dilution with water gave no precipitate of undiazotised amine. The solution was then poured into 1 litre of ice-water. A clear solution was produced, which after thirty seconds became cloudy and deposited a crystalline, brownish-yellow precipitate of the diazo-oxide (yield, 92 per cent.).

4-Nitronaphthalene-1-diazo-2-oxide was very sparingly soluble in water; it dissolved readily in benzene, acetone, or acetic acid, and

crystallised from these solvents. It was moderately soluble in alcohol, and on adding sodium hydroxide to this solution nitrogen was evolved and acetaldehyde produced.

With resorcinol, phloroglucinol, or 1:3-dihydroxynaphthalene the diazo-oxide reacted in alcoholic solution on the addition of a drop of aqueous sodium hydroxide, giving a blue coloration which can be used as a test for this diazo-derivative.

4-Nitronaphthalene-1-diazo-2-oxide has the remarkable property of coupling to form azo-compounds with the foregoing polyhydric phenols in a mixture of concentrated hydrochloric and acetic acids. It is, however, only with these very reactive phenols that this diazo-oxide has been found to combine.

#### *4-Nitro-β-naphthol-1-azoresorcinol (II).*

Five grams of 4-nitronaphthalene-1-diazo-2-oxide and 2·5 grams of resorcinol were dissolved in 50 c.c. of glacial acetic acid to which 5 c.c. of concentrated hydrochloric acid were added. After two days about 1 gram of the hydroxyazo-compound had separated, and on concentrating the filtrate a further 0·5 gram was obtained.

On pouring the filtrate into water, 5 grams of somewhat tarry azo-compound separated. The crystalline portions were crystallised repeatedly from glacial acetic acid, when the compound separated in reddish-black, nodular crystals melting at 254—256°:

0·1942 gave 20·25 c.c.  $N_2$  at 18° and 762 mm.  $N = 12·13$ .

$C_{16}H_{11}O_5N_3$  requires  $N = 12·92$  per cent.

*4-Nitro-β-naphthol-1-azoresorcinol* gave indigo-blue alkali salts in aqueous alkali hydroxides and developed an intense violet coloration with concentrated sulphuric acid. Although only sparingly soluble in water, this hydroxyazo-compound can be employed as an acid mordant dye. On unmordanted wool it furnished reddish-brown shades, becoming violet on subsequent treatment with copper sulphate and acetic acid. On chromium mordanted wool a bluish-black lake was produced. 4-Nitronaphthalene-1-diazo-2-oxide when coupled with phloroglucinol or 1:3-dihydroxynaphthalene in the presence of glacial acetic acid and concentrated hydrochloric acid gave rise to similar hydroxyazo-compounds dyeing chrome-mordanted wool in bluish-violet shades. Like the preceding substance these hydroxyazo-derivatives dissolved readily in the ordinary organic solvents, but showed very little tendency to crystallise. They gave rise to blue alkali salts and developed violet colorations with concentrated sulphuric acid.



*4-Nitro-β-naphthol (III).*

4-Nitronaphthalene-1-diazo-2-oxide (40 grams) was heated in a reflux apparatus with 600 c.c. of alcohol and 12 grams of finely divided copper for twelve hours. Acetaldehyde was evolved, and at the end of this period a drop of the solution tested with alkaline resorcinol no longer gave a blue coloration. This negative result indicated the absence of unaltered diazo-oxide, whereas the production of a red azo-dye with diazotised sulphanilic acid revealed the presence of a phenolic compound.

The filtered solution was evaporated to remove alcohol, and the residue extracted repeatedly with hot water. On cooling, the aqueous extracts furnished yellow, felted needles of 4-nitro-β-naphthol (yield about 38 per cent. of the theoretical). The copper precipitate contained an intensely coloured organic compound insoluble in alcohol, but dissolving in pyridine or aniline to a deep blue solution and in nitrobenzene to a purple solution. This product, owing to its insoluble, uncrystallisable nature, was not examined further.

Many experiments were carried out on the preparation of 4-nitro-β-naphthol, and it was found that other metals gave better results than copper in the reduction of the diazo-oxide.

With zinc dust (8 grams) and the foregoing proportions of diazo-oxide and alcohol the reduction was complete after boiling for sixteen hours, the yield of recrystallised 4-nitro-β-naphthol being 45 per cent. of the theoretical. The optimum result was obtained with powdered aluminium (7 grams) added to 70 grams of the diazo-oxide suspended in 1050 c.c. of alcohol. This mixture when heated under reflux for thirty-two hours gave a negative test with alkaline resorcinol, and after distilling off the alcohol and acetaldehyde and extracting the residue with hot water a yield of 58–64 per cent. of 4-nitro-β-naphthol was obtained.

This decomposition was effected in twenty-six hours by heating at 50° the diazo-oxide (64 grams) suspended in alcohol (1000 c.c.) with 24 c.c. of 30 per cent. hypophosphorous acid, the yield of 4-nitro-β-naphthol being 53 per cent.

In ethyl alcohol alone without metallic catalysts a yield of 45 per cent. of 4-nitro-β-naphthol was obtained after twenty-four hours' boiling. The replacement of ethyl by butyl alcohol lowered the yield considerably, as also did the employment of formic acid and copper powder.

After repeated crystallisation from carbon tetrachloride or benzene, 4-nitro-β-naphthol melted at 120°:

0.1810 gave 12 c.c.  $N_2$  at  $25^\circ$  and 768 mm.  $N=7.48$ .

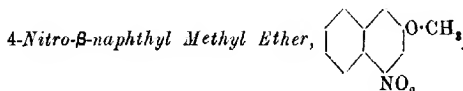
$C_{10}H_7O_3N$  requires  $N=7.41$  per cent.

4-Nitro- $\beta$ -naphthol crystallised from light petroleum (b. p.  $80-100^\circ$ ), hot water, or carbon tetrachloride in slender, yellow needles, and from benzene in compact, tabular prisms. It dissolved in aqueous alkali hydroxides to deep red solutions. Its potassium salt crystallised in glistening, red needles, but was hydrolysed on continued washing with water.

When reduced with tin and hydrochloric acid or with zinc dust and ammonium chloride in 50 per cent. alcohol, 4-nitro- $\beta$ -naphthol was reduced to 4-amino- $\beta$ -naphthol, but prolonged digestion on the water-bath with these reducing agents led to the elimination of the amino-group and the formation of 1:3-dihydroxynaphthalene (compare Friedländer, *Ber.*, 1895, **28**, 1952).

Attempts to convert 4-nitro- $\beta$ -naphthol into 4-nitro- $\beta$ -naphthylamine by heating under pressure with aqueous or alcoholic ammonia were not successful. It was not found possible to obtain a nitro-derivative of Meldola's blue by condensing 4-nitro- $\beta$ -naphthol with *p*-nitrosodimethylaniline hydrochloride in alcohol or acetic acid.

Experiments on alkylation showed that 4-nitro- $\beta$ -naphthol was much less reactive than  $\beta$ -naphthol. Boiling for twelve hours with alcohol containing 2 per cent. of sulphuric acid did not lead to ethylation of the nitro-compound.



The sodium salt of 4-nitro- $\beta$ -naphthol was suspended in dry xylene (10 parts) and boiled for eight hours with a slight excess of methyl sulphate. The solvent was evaporated, and the residue crystallised repeatedly from a mixture of benzene and alcohol:

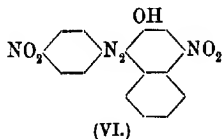
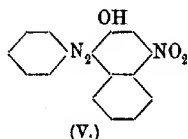
0.2227 gave 13.8 c.c.  $N_2$  at  $24^\circ$  and 760 mm.  $N=6.92$ .

$C_{11}H_9O_3N$  requires  $N=6.90$  per cent.

4-Nitro- $\beta$ -naphthyl methyl ether crystallised from a mixture of benzene and alcohol in lustrous, brown needles melting at  $100-103^\circ$ .

#### *Azo-derivatives of 4-Nitro- $\beta$ -naphthol.*

4-Nitro- $\beta$ -naphthol when dissolved in aqueous alkali hydroxides or carbonates coupled readily with various diazonium compounds.

*Benzene-1-azo-4-nitro-β-naphthol* (V),

A solution of benzenediazonium chloride added to 4-nitro- $\beta$ -naphthol (1 mol.) dissolved in  $N/2$ -sodium hydroxide gave at once an insoluble, dark red azo-compound which, after crystallisation from benzene, separated in dark brownish-red needles melting at  $206-207^\circ$ :

0.2088 gave 27.6  $N_2$  at  $22^\circ$  and 761.5 mm.  $N=14.98$ .

$C_{16}H_{11}O_3N_3$  requires  $N=14.33$  per cent.

Benzene-1-azo-4-nitro- $\beta$ -naphthol dissolved only sparingly in alcohol; it was insoluble in aqueous sodium hydroxide, in this respect resembling benzeneazo- $\beta$ -naphthol. The nitro-group had not rendered the compound acidic. Concentrated sulphuric acid developed a magenta coloration, whilst alcoholic sodium hydroxide gave a deep red solution.

*p*-Nitrobenzene-1-azo-4-nitro- $\beta$ -naphthol (VI).

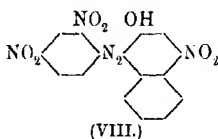
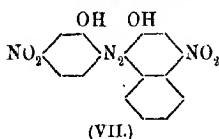
A dilute solution of *p*-nitrobenzenediazonium chloride added to 4-nitro- $\beta$ -naphthol dissolved in excess of  $N/2$ -sodium hydroxide gave a purplish-red precipitate of the azo-derivative difficult to crystallise on account of its sparing solubility in the ordinary solvents. From glacial acetic acid the azo-compound separated in nodular crystals melting at  $231^\circ$ :

0.1691 gave 23.5 c.c.  $N_2$  at  $17^\circ$  and 767.4 mm.  $N=16.29$ .

$C_{16}H_{10}O_5N_4$  requires  $N=16.57$  per cent.

*p*-Nitrobenzene-1-azo-4-nitro- $\beta$ -naphthol, which was insoluble in aqueous alkali hydroxides, dissolved in alcoholic sodium hydroxide to an intense purplish-blue solution probably containing a quinonoid sodium salt, hydrolysed by water with the regeneration of the original azo-compound. Concentrated sulphuric acid and this azo-compound developed a purple coloration.

When developed on calico padded with alkaline 4-nitro- $\beta$ -naphthol and Turkey red oil this azo-compound gave a crimson-red colour quite distinct from paranitroaniline-red. In this case deeper and more even shades were obtained when the 4-nitro- $\beta$ -naphthol was dissolved in aqueous sodium carbonate rather than in sodium hydroxide solution.

*Azo-4-nitro-β-naphthols from 2:4-Dinitroaniline,*

2:4-Dinitroaniline (3 grams) dissolved in cold concentrated sulphuric acid was diazotised as described on p. 1136, and the dilute acid solution of 2:4-dinitrobenzenediazonium sulphate added to a cold solution of 4-nitro-β-naphthol (1 mol.) dissolved in excess of normal sodium hydroxide. A dark reddish-brown precipitate *A* (3 grams) was at once produced, and the filtrate from this substance gave on acidification a paler red precipitate *B* (2 grams).

The former precipitate, *A*, which was probably a sodium salt, was boiled with glacial acetic acid to set free the azo-compound, which was then crystallised from anisole. The product separated in dark brownish-red, nodular crystals melting very indefinitely at 132–166°:

0.0738 gave 10.35 c.c.  $N_2$  at 26° and 764 mm.  $N=15.64$ .

$C_{11}H_{10}O_6N_4$  requires  $N=15.82$  per cent.

This analytical result corresponds with formula VII for a dihydroxyazo-compound which was probably precipitated in the form of its sparingly soluble sodium salt.

The second precipitate *B* also crystallised from anisole in dark red, tabular crystals with a green reflex. This product, when boiled with alcohol to remove the solvent, melted indefinitely between 200° and 250°:

0.2020 gave 31.7 c.c.  $N_2$  at 19° and 762.4 mm.  $N=18.09$ .

$C_{16}H_8O_7N_5$  requires  $N=18.28$  per cent.

This result corresponds with formula VIII for an azo-compound containing three nitro-groups. This azo-4-nitro-β-naphthol containing three nitro-groups is apparently acidic and remained dissolved until the alkaline solution was acidified. The two products of this azo-coupling were not very crystallisable, but the analytical data showed that the separation by means of alkali was practically complete.

With concentrated sulphuric acid, compound *A* (VII) gave a purple coloration, whereas compound *B* (VIII) developed an indigo-blue coloration.

*Azo-colouring Matters from 4-Nitro- $\beta$ -naphthol.*

The 4-nitro-derivative of orange II was prepared by adding diazotised sulphanilic acid to 4-nitro- $\beta$ -naphthol dissolved in excess of cold  $N/2$ -sodium hydroxide. On adding sodium chloride to the solution heated on the water-bath, the dye precipitated as a dark red powder, dyeing wool in deep red shades quite unlike those obtained from orange II.

*p*-Nitroaniline-*o*-sulphonic acid diazotised and coupled with alkaline 4-nitro- $\beta$ -naphthol gave an acid azo-dye furnishing orange shades on wool.

Picramic acid diazotised and coupled with 4-nitro- $\beta$ -naphthol furnished a dye melting above  $250^{\circ}$  and giving reddish-brown shades on unchromed wool, the chrome lake being brownish-purple. The three foregoing dyes gave deep red colorations with concentrated sulphuric acid.

Calico padded with 4-nitro- $\beta$ -naphthol, aqueous sodium carbonate, and Turkey-red oil was passed through a solution of sodium acetate and the bisdiazonium chloride from dianisidine. The fabric was dyed in dark blue shades.

Primuline dyed and diazotised on cotton gave with alkaline 4-nitro- $\beta$ -naphthol a purple maroon colour, quite unlike the red ingrain dye from  $\beta$ -naphthol.

Direct cotton colours dyeing in purple shades were obtained by coupling alkaline 4-nitro- $\beta$ -naphthol with the diazo-derivatives of safranine and 4:4'-diaminostilbene-2:2'-disulphonic acid.

*II. Diazotisation of 2:4-Dinitroaniline Sulphate.*

The 2:4-dinitroaniline employed in these experiments was obtained in practically quantitative yield by heating 4-chloro-1:3-dinitrobenzene with nine parts by weight of concentrated aqueous ammonia at  $110^{\circ}$  for two hours in the rotating autoclave.

In the following experiments, 2:4-dinitroaniline was diazotised in concentrated sulphuric acid. Dry sodium nitrite (2.2 grams) was added to 7.5 c.c. of cold concentrated sulphuric acid, and the mixture heated to  $75^{\circ}$ . The clear liquid thus obtained was cooled in ice, and 5 grams of 2:4-dinitroaniline were added with stirring. After two hours, the pasty mass was diluted to 700 c.c. with ice and water. The solution at this stage contained 2:4-dinitrobenzenediazonium sulphate, as was proved by adding the liquid slowly to alkaline  $\beta$ -naphthol, when 2:4-dinitrobenzeneazo- $\beta$ -naphthol was deposited as a bright orange-red precipitate very sparingly soluble in the ordinary organic media. This product

crystallised from hot glacial acetic acid in orange-red needles, and did not melt below 270°. With cold concentrated sulphuric acid it developed a purple-blue coloration, and with alcoholic sodium hydroxide a deep blue solution.

*5-Nitro-2-diazophenol.*

Elimination of the ortho-nitro-group in 2:4-dinitrobenzene-diazonium sulphate was effected by pouring the diazo-solution, prepared as in the foregoing diazotisation, into a litre of water containing 17.4 grams of sodium carbonate and 400 grams of ice. After one hour, a yellow precipitate was collected which, on drying at the ordinary temperature, weighed 0.7 gram. The insoluble product, which melted and decomposed between 64° and 80°, coupled with alkaline  $\beta$ -naphthol, yielding a purplish-brown azo-compound. When half the amount of water was used in the neutralisation, the amount of this by-product increased to 0.9 gram.

The yellow, alkaline solution from this by-product was added to excess of alkaline  $\beta$ -naphthol, when the yellow colour of the 5-nitrodiazophenol disappeared, and a deep blue precipitate with bronze reflex was produced, the supernatant liquid having a brown tint. This blue compound was a sparingly soluble sodium salt which, on treatment with alcoholic hydrogen chloride, yielded a purplish-red azo- $\beta$ -naphthol melting at 228°, and identical with the 4-nitro-2-hydroxybenzeneazo- $\beta$ -naphthol obtained from the internal diazo-oxide of 5-nitro-2-aminophenol (T., 1915, **107**, 655). The identity of the two compounds was confirmed by a mixed melting-point determination and by the formation of the characteristic metallic lakes from the foregoing preparation.

The production of a dihydroxyazo-compound from  $\beta$ -naphthol and the alkaline solution of the diazo-derivative of 2:4-dinitroaniline showed that in alkaline solution the ortho-nitro-group had been replaced by hydroxyl. This conclusion was confirmed by the following experiments.

*5-Nitrophenol-2-resorcinol (IV).*

Sodium nitrite (1.1 grams) was added to 3.75 c.c. of concentrated sulphuric acid, the temperature being kept below 70°. The warm solution was cooled, and 2.5 grams of 2:4-dinitroaniline were added. After one hour, the brown paste was added to a solution of 8.8 grams of sodium carbonate in 300 c.c. of water containing 100 grams of ice.

The yellow solution filtered from the insoluble by-product (0.4

gram) was treated with 1.5 grams of resorcinol in 5.7 c.c. of 20 per cent. aqueous sodium hydroxide. The intense purplish-red alkaline solution was subsequently warmed on the water-bath, and the sodium salt of the azo-dye precipitated by the addition of 100 grams of sodium chloride. This sodium salt (4.5 grams) gave the orange-red azo-resorcinol on treatment with dilute sulphuric acid. When crystallised from glacial acetic acid, it separated in small, reddish-brown needles decomposing at 225°. The sulphuric acid coloration was deep red:

0.0997 gave 13.75 c.c.  $N_2$  at 21.5° and 762 mm.  $N = 15.67$ .

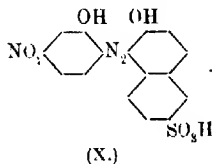
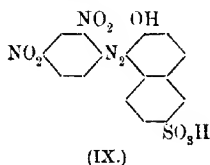
$C_{12}H_9O_5N_3$  requires  $N = 15.27$  per cent.

The percentage of nitrogen required for dinitrobenzeneazo-resorcinol is 18.42.

On unchromed wool, this azo-resorcinol gave bright orange-red shades, changing to deep claret on chroming subsequently with 1 per cent. of chromic acid. By the metachrome process of dyeing, very deep purple shades were produced, appearing almost black.

The marked alteration of shade produced by mordanting with chromium suggested the arrangement of two hydroxyl groups contiguous to the azo-group, as indicated in the above formula. Further evidence was obtained, by a comparative experiment made on  $\beta$ -naphthol-6-sulphonic acid.

*Azo-dyes from 2:4-Dinitroaniline and Schäffer's Acid.*



(1) 2:4-Dinitroaniline (2.5 grams) was added to a solution of 1.1 grams of sodium nitrite in 7.5 c.c. of concentrated sulphuric acid, and the resulting paste added to 150 c.c. of cold water. This acid solution of 2:4-dinitrobenzenediazonium sulphate was added to 3.5 grams of Schäffer's salt dissolved in 100 c.c. of water and 70 c.c. of 5*N*-sodium hydroxide. After one hour, the solution was heated on the water-bath and the azo-dye precipitated with 50 grams of salt. This dye, 2:4-dinitrobenzeneazo- $\beta$ -naphthol-6-sulphonic acid (IX), gave orange shades on unmordanted wool not altered by chroming.

(2) 2:4-Dinitroaniline (2.5 grams) was diazotised as before in concentrated sulphuric acid; the diluted diazo-solution was

rendered alkaline with excess of aqueous sodium carbonate and added to an alkaline solution of Schäffer's salt. After one hour, the solution was warmed and the dye precipitated with sodium chloride. This dye, 4-nitro-2-hydroxybenzeneazo- $\beta$ -naphthol-6-sulphonic acid (X), gave reddish-brown shades on wool, changing to deep violet on chroming.

(3) The dinitroaniline (2.5 grams) was diazotised as before, and to the dilute acid solution was added 3.4 grams of copper sulphate; the liquid was then rendered alkaline with sodium carbonate and added to an alkaline solution of Schäffer's salt. Coupling occurred slowly, and was completed by warming, the dye being then salted out. It gave purple shades on wool, which were not affected by after-chroming. These purple shades were reproduced by treating the dyed patterns of the second preparation with copper sulphate. Similar purple shades were obtained by treating the dihydroxyazo-dye (X) with cobalt chloride or chlorocobaltipentammine chloride,  $[\text{Co}(\text{NH}_3)_5]\text{Cl}_2$ .

These experiments point conclusively to the formation of a soluble form of 5-nitro-2-diazophenol when an acid solution of 2:4-dinitrobenzenediazonium sulphate is rendered alkaline with sodium carbonate.

The azo-dyes produced by coupling this alkaline diazo-solution with various phenolic derivatives and reactive amines all have the property of forming distinctly coloured metallic lakes. With 2:4-tolylenediamine, the aminohydroxyazo-dye was produced in dilute acetic acid. In the case of the aminonaphtholsulphonic acids, the coupling was effected in the presence of sodium hydroxide. With chromotropic acid, the most favourable result was obtained on using milk of lime as the alkali.

*Azo-dyes from 5-Nitro-2-diazophenol.*

| Coupling substance.  | Colour of dye on unmordanted wool. | Colour of mordanted dye.                                 |
|--|------------------------------------|--|
| 2:4-Tolylenediamine.   | —                                  | { Metachrome process: purplish-black lake (1 per cent.). |
| 2-Hydroxy-3-naphthoic acid.  | Reddish-brown.                     | Purple chromium lake.                                    |
| 1:8-Dihydroxynaphthalene-3:6-disulphonic acid (chromotropic acid). | Bluish-red.                        | { Chromium—greenish-blue.<br>Vanadium—blue.              |
|  |                                    | { Copper—bluish-purple.<br>Cobalt—purplish-blue.         |
| 8-Amino-2-naphthol-3:6-disulphonic acid (H acid).                  | Purple.                            | { Chromium—dark green.<br>Vanadium—green.                |
|  |                                    | { Copper—intense blue.<br>Cobalt—dark bluish-purple.     |



*Azo-dyes from 5-Nitro-2-diazophenol (continued).*

| Coupling substance.   | Colour of dye<br>on unmordanted<br>wool. | Colour of mordanted dye.   |
|---|--|--|
| 8 - Amino - $\alpha$ - naphthol -<br>5-sulphonic acid (S acid). } | Mauve.                                   | Chromium—sage-green.<br>Vanadium—bright green.<br>Copper—bright blue.<br>Cobalt—blue.<br>Nickel—blue.<br>Iron—dull violet.<br>Manganese—dull violet.<br>Uranium—dark lavender<br>blue. |
| 7 - Amino - $\alpha$ - naphthol -<br>3-sulphonic acid (J acid). } | Crimson-red.                             | Chromium—dark bluish-<br>grey.<br>Vanadium—dark purplish-<br>blue.<br>Copper—purple.<br>Cobalt—maroon.<br>Uranium—maroon.  |

The foregoing azo-colouring matters when dyed on unmordanted wool are extremely sensitive to metals, this property being due, undoubtedly, to the ease with which the metallic lakes are produced.

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[Received, August 7th, 1919.]

*C.— $\beta$ -Naphthylmethylamine.*

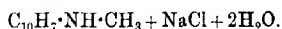
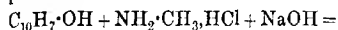
By GILBERT T. MORGAN and FREDERICK PAGE EVENS.

$\beta$ -NAPHTHYLMETHYLAMINE, the simplest alkyl derivative of  $\beta$ -naphthylamine, has not hitherto received detailed attention, probably owing to the circumstance that it is not produced readily by the action of ordinary methylating agents on the primary base.

Powerful methylating agents, such as methyl iodide in excess, lead to quaternary ammonium salts, from which the quaternary ammonium hydroxide and  $\beta$ -naphthyldimethylamine are successively obtained (Hantzsch, *Ber.*, 1880, **13**, 2054; Bamberger, *ibid.*, 1889,

**22**, 1306). By operating with equal weights of  $\beta$ -naphthylamine and methyl iodide at  $100^\circ$  in methyl-alcoholic solution, von Pechmann and Heinze produced a certain proportion of  $\beta$ -naphthylmethylamine, which, however, required purification by conversion into its nitrosoamine and subsequent reduction, so that the yield of recovered base was not satisfactory (*Ber.*, 1895, **28**, 2370; 1897, **30**, 1785). Pschorr and Karo subsequently obtained the base by the action of methyl sulphate on benzenesulphon- $\beta$ -naphthalide and subsequent hydrolysis of the product (*Ber.*, 1906, **39**, 3142).

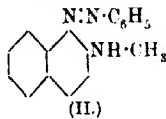
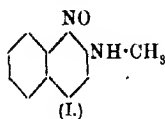
It has now been found that  $\beta$ -naphthylmethylamine can be prepared in excellent yield and in a state of purity by the interaction of  $\beta$ -naphthol and aqueous methylamine at high temperatures under pressure.



$\beta$ -Naphthol (100 grams), methylamine hydrochloride (75 grams), and 190 c.c. of 5*N*-sodium hydroxide were heated in a rotating steel autoclave at  $200$ – $220^\circ$  for seven hours, the pressure attained being about 21 kilos. per sq. cm. The oily contents of the autoclave were extracted successively with aqueous sodium hydroxide to remove unaltered  $\beta$ -naphthol, and with benzene to dissolve  $\beta$ -naphthylmethylamine. The benzene extract, after drying over calcium chloride, was distilled first under the ordinary and then under diminished pressure, the yield of secondary base being upwards of 80 per cent. of the theoretical.

$\beta$ -Naphthylmethylamine boiled at  $317^\circ/766$  mm. and at  $207^\circ/60$  mm., and when freshly distilled was colourless, but darkened rapidly on exposure to the air. It was identified by its solid nitrosoamine, which crystallised in pale yellow needles and melted at  $88^\circ$  (Pechmann gives  $90^\circ$ ; Pschorr and Karo,  $88$ – $89^\circ$ ).

1-Nitroso- $\beta$ -naphthylmethylamine (I).



$\beta$ -Naphthylmethylnitrosoamine (5 grams) was suspended in 20 c.c. of alcohol, and 20 c.c. of saturated alcoholic hydrogen chloride were slowly added with vigorous stirring at  $0^\circ$ . The nitrosoamine partly dissolved and the solution darkened. After twenty hours, a few dark green crystals had separated, and the mixture was poured into water. The hydrochloride of the nitroso-

base dissolved, whereas unaltered nitrosoamine was precipitated. On adding aqueous ammonia to the filtrate, the nitroso-base separated, and was crystallised from acetone, when it was obtained in dark green plates melting at  $142^{\circ}$ :

0.1041 gave 13.5 c.c.  $N_2$ \* at  $17^{\circ}$  and 753 mm.  $N=14.95$ .

$C_{11}H_{10}ON_2$  requires  $N=15.05$  per cent.

The optimum yield of 1-nitroso- $\beta$ -naphthylmethylamine obtained by the foregoing process was 75 per cent. of the theoretical. Unlike  $\beta$ -naphthylmethylnitrosoamine, this nitroso-base gave no Liebermann reaction. The conversion of 1-nitroso- $\beta$ -naphthylmethylamine into the anhydro-base (methenyl-1:2-naphthylene-diamine),  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} > CH$ , did not proceed smoothly by the method of O. Fischer and Hepp, employed in the case of the ethenyl analogue (*Ber.*, 1887, 20, 2471), but when the nitroso-base was heated in alcoholic hydrogen chloride at  $100^{\circ}$  in a sealed tube, the hydrochloride of the anhydro-base separated in reddish-white crystals.

#### *Azo-derivatives of $\beta$ -Naphthylmethylamine.*

The azo-derivatives of  $\beta$ -naphthylmethylamine were prepared by two general methods, namely, (1) interaction of the base and diazonium salts, and (2) condensation of  $\beta$ -naphthylmethylnitrosoamine with primary aromatic amines.

#### *Benzeneazo- $\beta$ -naphthylmethylamine (II).*

The diazonium chloride from 1 gram of aniline was added in aqueous solution to  $\beta$ -naphthylmethylamine (1.7 grams) dissolved in cold dilute hydrochloric acid; a crimson coloration developed, and the addition of sodium acetate induced coagulation of the azo-compound. The viscid precipitate was dissolved in hot alcohol, from which the product crystallised in felted, scarlet needles melting at  $82-83^{\circ}$  (quantitative yield):

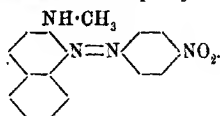
0.1176 gave 16.6 c.c.  $N_2$  at  $18^{\circ}$  and 750 mm.  $N=16.14$ .

$C_{17}H_{15}N_3$  requires  $N=16.09$  per cent.

Benzeneazo- $\beta$ -naphthylmethylamine was also obtained in satisfactory yield on warming a glacial acetic acid solution of  $\beta$ -naphthylmethylnitrosoamine and aniline in molecular proportions.

The product, which was precipitated on diluting the acetic acid solution with water, was identical with the foregoing preparation.

\* In this and the following nitrogen estimations the gas was measured over 33 per cent. aqueous potassium hydroxide.

*p*-Nitrobenzene-1-azo- $\beta$ -naphthylmethylamine,

An acid solution of *p*-nitrobenzenediazonium chloride (1 mol.) was added to  $\beta$ -naphthylmethylamine (1 mol.) dissolved in dilute hydrochloric acid, the temperature being below  $6^{\circ}$ . Sodium acetate precipitated the azo-compound in quantitative yield. The reddish-brown product was crystallised from ethyl acetate, acetone, benzene, or glacial acetic acid; it separated in matted, dark brown needles with bronze reflex, and melted at  $190-192^{\circ}$ :

0.0977 gave 15.1 c.c.  $N_2$  at  $15.5^{\circ}$  and 750 mm.  $N=17.85$ .

$C_{17}H_{14}O_2N_4$  requires  $N=18.30$  per cent.

*p*-Nitrobenzeneazo- $\beta$ -naphthylmethylamine was also produced by warming together in glacial acetic acid molecular proportions of *p*-nitroaniline and  $\beta$ -naphthylmethylnitrosoamine.

Like the preceding compound, this azo-derivative developed an intense violet coloration with concentrated sulphuric acid.

*Azo-dyes from  $\beta$ -Naphthylmethylamine.*

These azo-colouring matters can be obtained by the two general methods outlined in the foregoing preparations.

| Diazo-derivative of amino-acid.                                  | Tinctorial properties of the resulting dye.  | Coloration in concentrated sulphuric acid. |
|--|--|--|
| 1. Sulphanilic acid.   | Scarlet on wool.   | Reddish-blue.                              |
| 2. Naphthionic acid.   | Dark red on wool.  | Dark violet.                               |
| 3. Picramic acid :<br>Direct dye.<br>Dyed by metachrome process. | Dull purple on wool.<br>After prolonged boiling (8 hours) a dark purple unlike the analogous dye from $\beta$ -naphthylamine, which changes to olive-green shades. | Reddish-brown.                             |
| 4. Diaminostilbenedisulphonic acid.                              | Purple on unmordanted cotton much bluer in shade than Hessian Purple N. from $\beta$ -naphthylamine.   | Greenish-blue.                             |

*Acyl Derivatives of  $\beta$ -Naphthylmethylamine.*

Aceto- $\beta$ -naphthylmethylamide,  $C_{10}H_7N(CH_3)CO\cdot CH_3$ , was prepared by mixing  $\beta$ -naphthylmethylamine (1 mol.) and acetic

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anhydride (1.5 mols.). The product when crystallised from light petroleum (b. p. 40—60°) separated in colourless, rhombic prisms melting at 50—51°:

0.1523 gave 9.6 c.c.  $N_2$  at 16° and 751.5 mm.  $N=7.28$ .

$C_{13}H_{13}ON$  requires  $N=7.04$  per cent.

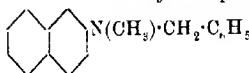
*Benzo- $\beta$ -naphthylmethylanide*,  $C_{10}H_7N(CH_3)CO \cdot C_6H_5$ , produced by the Schotten-Baumann reaction, crystallised from light petroleum in colourless needles melting at 84°:

0.2663 gave 11.3 c.c.  $N_2$  at 20° and 762 mm.  $N=4.88$ .

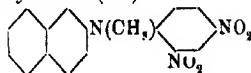
$C_{18}H_{15}ON$  requires  $N=5.36$  per cent.

*Toluene-*p*-sulphon- $\beta$ -naphthylmethylanide*.—This compound, which has already been described as resulting from the methylation of toluene-*p*-sulphon- $\beta$ -naphthylanide (Morgan and Micklethwait, T., 1912, 101, 150), was prepared more directly by grinding together  $\beta$ -naphthylmethylanine, toluene-*p*-sulphonyl chloride, and fused sodium acetate in approximately molecular proportions. The crude product, after digestion with aqueous sodium carbonate, was crystallised from alcohol, and separated in colourless, arborescent needles melting at 73° (T., 1912, *ibid.*, colourless needles, m. p. 77—78°).

*Benzyl- $\beta$ -naphthylmethylanine* (III).



(III.)



(IV.)

$\beta$ -Naphthylmethylanine (1 mol.) and benzyl chloride (1.25 mols.) were mixed and heated with 10 per cent. aqueous sodium hydroxide (1.25 mols.) in a reflux apparatus for several hours until the solid product of the mixture of the two organic reagents had been decomposed. On cooling, a brown, solid mass separated consisting of crude benzyl- $\beta$ -naphthylmethylanine (yield, 70 per cent.). This base was soluble in benzene, acetone, or alcohol, and crystallised in lustrous, colourless needles melting at 82—83°:

0.3358 gave 15.8 c.c.  $N_2$  at 17° and 765 mm.  $N=5.51$ .

$C_{18}H_{17}N$  requires  $N=5.67$  per cent.

Like all the other known dialkyl- $\beta$ -naphthylamines, this tertiary base did not couple with diazonium salts.

*2:4-Dinitrophenyl- $\beta$ -naphthylmethylanine* (IV).

Molecular proportions of  $\beta$ -naphthylmethylanine and 4-chloro 1:3-dinitrobenzene were dissolved in alcohol, and the solution was

heated under reflux with fused sodium acetate for two to three hours. The crystalline product separating from the cooled solution was washed successively with alcohol and water to remove 4-chloro-1:3-dinitrobenzene and sodium salts respectively. The final residue was crystallised from benzene or acetic acid, from which it separated in orange-red, elongated prisms melting at  $183^{\circ}$ :

0.1630 gave 18.2 c.c.  $N_2$  at  $18^{\circ}$  and 756 mm.  $N=12.88$ .

$C_{17}H_{18}O_4N_3$  requires  $N=13.00$  per cent.

2:4-Dinitrophenylnitro- $\beta$ -naphthylmethylamine,

$NO_2 \cdot C_{10}H_6 \cdot N(CH_3) \cdot C_6H_3(NO_2)_2$ .

—The preceding dinitro-compound was dissolved in the least possible amount of glacial acetic acid and treated with sufficient nitric acid (D 1.42), diluted with an equal volume of glacial acetic acid, to introduce one nitro-group. The solution was stirred thoroughly, warmed, and left overnight in the ice-chest, when a mass of yellow crystals separated. This product crystallised from alcohol in yellow flakes and melted at  $156-157^{\circ}$ :

0.1080 gave 14.7 c.c.  $N_2$  at  $22^{\circ}$  and 761 mm.  $N=15.52$ .

$C_{17}H_{12}O_6N_4$  requires  $N=15.22$  per cent.

The authors' thanks are due to the British Dyestuffs Corporation (Manchester) for the starting materials employed in this investigation.

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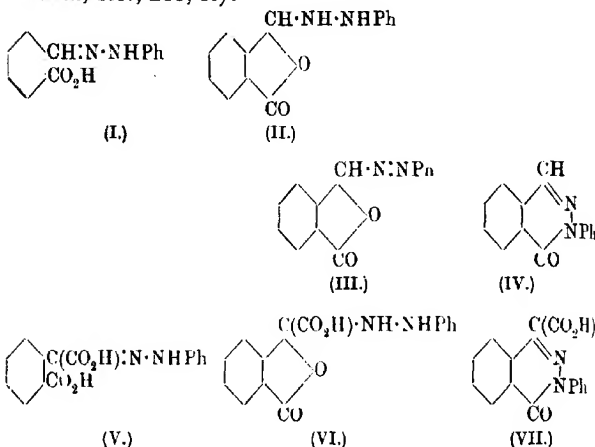
# CL.—Action of Phenylhydrazine on Phthalaldehydic and Phthalonic Acids: Phenyl-hydrazo- and Azo-Phthalide.

By PRAPULLA CHANDRA MITTER and JNANENDRA NATH SEN.

In a previous communication (T., 1917, 111, 988) the authors have shown that by the action of phenylhydrazine on opianic and nitro-opianic acids in ethereal solution derivatives of hydrazophthalide are formed, which can be oxidised by mercuric oxide to azo-phthalides. In the case of phthalonic acid definite indications of the formation of hydrazo- and azo-phthalide derivatives were obtained, although the products could not then be isolated. It has

now been found that on adding a solution of phenylhydrazine hydrochloride to a nearly neutral solution of phthalonic acid the phenylhydrazone is obtained, which on treatment with dilute hydrochloric acid is converted into phenylphthalazonecarboxylic acid identical with the anhydrophenylhydrazine-*o*-carboxyphenylglyoxylic acid prepared by Henriques (*Ber.*, 1888, **21**, 1610).

In the case of phthalaldehydic acid, treatment with phenylhydrazine hydrochloride under similar conditions gives phenylhydrazophthalide, which can be oxidised in acetone solution by mercuric acetamide to phenylazophthalide. Treatment with acetic acid converts the hydrazophthalide into phenylphthalazone (Racine, *Annalen*, 1887, **239**, 80):



#### EXPERIMENTAL.

##### *Phenylhydrazone of Phthalaldehydic Acid (I).*

On account of the great solubility of the phenylhydrazine derivative in ether, the compound was prepared by the action of phenylhydrazine hydrochloride on the sodium salt of phthalaldehydic acid.

Phthalaldehydic acid (1.5 grams: 1 mol.) was dissolved in sodium carbonate solution (0.75 mol.), and to this an aqueous solution of phenylhydrazine hydrochloride (1.45 grams: 1 mol.) was added. The phenylhydrazine derivative separated almost immediately as a canary-yellow powder in almost quantitative yield (2.7 grams). On crystallisation from slightly warm dilute alcohol it was obtained in pale yellow needles melting at 106°, which turned pink on exposure

to air. It dissolves readily in sodium hydrogen carbonate solution or ammonia. Acetic acid transforms it into the cyclic compound:

0.1065 gave 0.2741  $\text{CO}_2$  and 0.0476  $\text{H}_2\text{O}$ .  $\text{C}=70.19$ ;  $\text{H}=4.97$ .

0.1011 „ 10.3 c.c.  $\text{N}_2$  at  $24^\circ$  and 760 mm.  $\text{N}=11.79$ .

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{C}=70.00$ ;  $\text{H}=5.00$ ;  $\text{N}=11.66$  per cent.

The substance was dissolved in alcohol and titrated with standard alkali. It was found to be monobasic:

0.1373 required 5.65 c.c. of  $\text{N}/10$ -alkali, whilst this weight of a monobasic acid of the above formula requires 5.70 c.c.

*Phenylazophthalide.*

Phenylhydrazophthalide (II, 0.55 gram) was dissolved in about 20 c.c. of pure acetone, 2 grams of pure recrystallised mercuric acetamide were added, and the mixture was heated on the water-bath under reflux for about three hours. The colour of the solution gradually changed to deep yellow. The solution was filtered, the residue washed with acetone, and the washings added to the filtrate. The filtrate was evaporated to dryness and the residue washed with dilute sodium carbonate solution and water, and then dissolved in acetone. On adding water a small quantity of tarry matter was precipitated, which was removed by filtration. Further addition of water precipitated the azo-compound (III) in yellow plates melting at  $149-150^\circ$ . The substance is insoluble in sodium carbonate, and gives with concentrated sulphuric acid a purple coloration. The alcoholic solution is yellow with a green shade, and the colour changes to pink on the addition of alkali.

The compound dissolves readily in acetone or benzene:

0.1581 gave 0.4132  $\text{CO}_2$  and 0.0612  $\text{H}_2\text{O}$ .  $\text{C}=71.05$ ;  $\text{H}=4.30$ .

0.1025 „ 10.5 c.c.  $\text{N}_2$  at  $24^\circ$  and 760 mm.  $\text{N}=11.86$ .

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2$  requires  $\text{C}=70.49$ ;  $\text{H}=4.20$ ;  $\text{N}=11.77$  per cent.

*Phenylphthalazone (IV).*

Phenylhydrazophthalide is warmed with a small quantity of glacial acetic acid for a few minutes and hot water is added. The phthalazone is readily obtained in fine needles with a pale pink colour melting at  $105^\circ$ . It is insoluble in alkali even on boiling. (Found:  $\text{N}=13.11$ .  $\text{C}_{14}\text{H}_{10}\text{ON}_2$  requires  $\text{N}=12.61$  per cent.)

*Phthalonic Acid and Phenylhydrazine.*

Phthalonic acid (1 gram: 1 mol.) was dissolved in water containing sodium carbonate (0.42 gram: 0.75 mol.), and a solution of



phenylhydrazine hydrochloride (1.5 grams: 2 mols.) in water was added. The phenylhydrazine derivative (V or VI) separated at once in crystalline flakes melting at 171—172°. It dissolves readily in acetone or alcohol, but on the addition of water the solution deposits an oil. All attempts at recrystallisation failed:

0.0938 gave 0.2167 CO<sub>2</sub> and 0.0360 H<sub>2</sub>O. C=63.06; H=4.27.

0.1169 „ 9.6 c.c. N<sub>2</sub> at 23° and 760 mm. N=9.73.

C<sub>15</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub> requires C=63.38; H=4.23; N=9.85 per cent.

The substance was dissolved in dilute alcohol and titrated with standard alkali. It was found to be dibasic:

0.1449 required 9.4 c.c. of N/10-alkali, whilst this weight of a dibasic acid of the above molecular formula requires 10.2 c.c.

The substance gradually turns brownish-yellow on exposure to air. Attempts at oxidation with mercuric acetamide did not yield any pure product.

*Phenylphthalazonecarboxylic Acid (VII).*

The mother liquor after the filtration of the hydrazo-compound deposits, on keeping, long needles with a silky lustre dissolving readily in sodium carbonate solution and melting at 210°. The same substance is also obtained by keeping the hydrazophthalidicarboxylic acid suspended in dilute hydrochloric acid. (Found, C=67.08; H=3.63; N=10.10. C<sub>15</sub>H<sub>10</sub>O<sub>3</sub>N<sub>2</sub> requires C=67.67; H=3.76; N=10.05 per cent.

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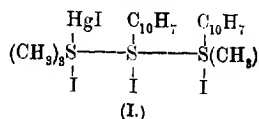
CII.—*Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. Part VII. Chain Compounds of Sulphur (continued).*

By SIR PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA.

IN Part IV. of this series (this vol., p. 261), among the products of the interaction of phenyl mercaptan and mercuric nitrite which were isolated, was one having the empirical formula Ph<sub>2</sub>S<sub>3</sub>Hg. When α-naphthyl mercaptan is treated with mercuric nitrite only one product is obtained, which is the exact analogue of the former, namely, (C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>S<sub>3</sub>Hg. This, like the benzenoid derivative, is

soluble in hot benzene, and can therefore be easily obtained in a state of purity.

The action of methyl iodide on the compound  $\text{Ph}_3\text{S}_3\text{Hg}$  leads to a trisulphonium compound in which all the sulphur atoms are quadrivalent (compare Part IV.). The action of alkyl iodides on the new compound,  $(\text{C}_{10}\text{H}_7)_2\text{S}_3\text{Hg}$ , has proved to be of much interest. With methyl iodide, for instance, three sulphonium derivatives, tri-, di-, and mono-, are formed together. The trisulphonium compound (I) contains two sexavalent and one quadrivalent sulphur atoms. The

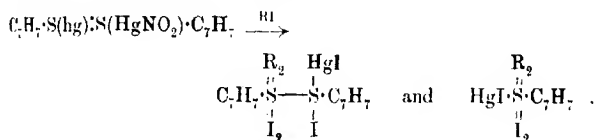


monosulphonium derivative also contains a sexavalent sulphur atom, and all the monosulphonium compounds described in the present paper are of this category.

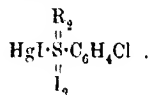
The action of *p*-tolyl mercaptan on mercuric nitrite has also been studied. The mercaptide nitrite corresponds with the formula  $\text{C}_7\text{H}_7\cdot\text{S}(\text{hg})(\text{HgNO}_2)\cdot\text{S}\cdot\text{C}_7\text{H}_7$ , or preferably  $\text{C}_7\text{H}_7\cdot\text{S}(\text{hg})\text{:S}(\text{HgNO}_2)\cdot\text{C}_7\text{H}_7$ .

*p*-Chlorophenyl mercaptan also yields a compound of exactly the same type. That they are definite compounds is proved by the fact that successive crops from hot benzene solution have the same melting point and composition.

The mercaptide nitrite obtained from *p*-tolyl mercaptan reacts with methyl and ethyl iodides, yielding in each case a mono- and a disulphonium compound, the sulphur atoms of the latter being sexavalent (compare Part VI., this vol., p. 548):



The mercaptide nitrite from *p*-chlorophenyl mercaptan gives with alkyl iodides only one monosulphonium compound of the type:



In Part VI. of this series one of us has described disulphonium compounds containing one or both of the atoms of sulphur in the

sexavalent condition. The present work not only corroborates the existence of this class of compounds, but goes a step further in that a trisulphonium compound is described containing two sexavalent and one quadrivalent sulphur atoms.

In addition to the monosulphonium compounds described in the present paper, another series has been prepared, namely, that obtained by the reaction of ethyl sulphide and mercuric iodide with the higher and lower homologues of ethyl iodide, and in each case a compound of the type  $\text{Et}_2\text{S} \cdot \text{RI} \cdot \text{HgI}_2$  has been obtained (compare Smiles and Hilditch, T., 1907, 91, 1396).

It has already been shown that the disulphonium compounds can be synthesised by the direct union of the components, for example, ethyl disulphide, ethyl iodide, and mercuric iodide (T., 1916, 109, 611). By substituting, however, the other alkyl iodides the corresponding members of the series have been obtained, with this difference, that an interchange of radicles invariably takes place. Thus, when a mixture of ethyl disulphide and mercuric iodide is treated with an alkyl iodide,  $\text{RI}$ , compounds of the type  $\text{EtRS}_2 \cdot \text{HgI}_2 \cdot \text{RI}$  are formed. Again, when a mercaptide nitrite like the compound  $\text{EtS} \cdot \text{HgNO}_2$  is treated with an alkyl iodide,  $\text{RI}$ , by an interchange of radicles, the compound  $\text{EtRS}_2 \cdot \text{HgI}_2 \cdot \text{RI}$  is obtained (*loc. cit.*). It is thus seen that either mode of formation yields the same compound, the interchange of radicles being thus the most prominent feature. There is, however, this marked difference that in the monosulphonium series no such interchange of radicles has been found to take place.

#### EXPERIMENTAL.

##### *Interaction of $\alpha$ -Naphthyl Mercaptan and Mercuric Nitrite:*

##### *Formation of the Compound $(\text{C}_{10}\text{H}_7)_2\text{S}_3\text{Hg}$ .*

An alcoholic solution of  $\alpha$ -naphthyl mercaptan was slowly dropped from a pipette into mercuric nitrite solution with constant shaking. At first a white precipitate appeared, which, however, soon acquired a yellow tint. The granular precipitate was collected, washed, and dried in a vacuum. For further purification it was crystallised from boiling benzene, in which it was fairly readily soluble, and then melted at  $193^\circ$ :

0.1118 gave 0.1827  $\text{CO}_2$  and 0.0344  $\text{H}_2\text{O}$ .  $\text{C}=44.57$ ;  $\text{H}=3.43$ .

0.1200 "., 0.0459  $\text{Hg}$  and 0.1354  $\text{BaSO}_4$ .  $\text{Hg}=37.93$ ;  $\text{S}=15.32$ .

$\text{C}_{20}\text{H}_{14}\text{S}_3\text{Hg}$  requires  $\text{C}=43.63$ ;  $\text{H}=2.54$ ;  $\text{Hg}=36.36$ ;

$\text{S}=17.45$  per cent.

*Interaction of the Compound  $(C_{10}H_7)_2S_3Hg$  and Methyl Iodide:  
Formation of the Trisulphonium Compound (I).*

The method of procedure is exactly the same as in the interaction of simple mercaptide nitrites and alkyl iodides. After heating with methyl iodide under reflux, the mixture was allowed to cool. Within half an hour, the heavy, oily liquid at the bottom began to solidify to well-defined crystals, which were collected. The substance was insoluble in acetone, and was therefore washed several times with this solvent. Finally, it was recrystallised from hot methyl alcohol, when dull yellow crystals melting at  $113^\circ$  were obtained. Both the soluble and insoluble varieties of this series of sulphonium compounds dissolve readily in boiling methyl alcohol, and thus all of them have been obtained in a pure condition:

0.2196 gave 0.2219  $CO_2$  and 0.0574  $H_2O$ .  $C=27.56$ ;  $H=2.90$ .  
 0.3016 „ 0.0540  $Hg$  „ 0.2484  $AgI$ .  $Hg=17.91$ ;  $I=44.15$ .  
 0.3729 „ 0.2223  $BaSO_4$ .  $S=8.19$ .

$C_{26}H_{32}I_4S_3Hg$  requires  $C=27.18$ ;  $H=2.79$ ;  $Hg=17.42$ ;  
 $I=44.26$ ;  $S=8.36$  per cent.

The filtrate, after the separation of the above insoluble compound, was freed from excess of methyl iodide by evaporation. The oily residue was dissolved in acetone, the solution filtered, concentrated to a small bulk, and excess of ether added, when a yellow oil was again precipitated. The oil was dissolved in boiling methyl alcohol, and on slowly cooling, yellow needles with a faint green tint separated. From the methyl alcoholic solution five successive crops were obtained by fractional crystallisation. Of these, the first two crops melted at  $102^\circ$ ; they were therefore mixed and again crystallised from the above solvent, when the product melted at the same temperature. This was the sexavalent monosulphonium compound and gave the following results on analysis:

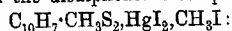
0.1496 gave 0.1058  $CO_2$  and 0.0284  $H_2O$ .  $C=19.29$ ;  $H=2.11$ .  
 0.3927 „ 0.1023  $Hg$  „ 0.3524  $AgI$ .  $Hg=26.05$ ;  $I=48.48$ .  
 0.2650 „ 0.0693  $Hg$ .  $Hg=26.12$ .

$C_{12}H_{13}I_3SHg$  requires  $C=18.7$ ;  $H=1.82$ ;  $Hg=25.97$ ;  
 $I=49.5$  per cent.

The mother liquor from which the above five fractions were obtained began to deposit oily globules which were dissolved in acetone. On the addition of ether an oil was obtained which was kept in a vacuum over sulphuric acid for several days, but did not solidify. On stirring, however, with a little ether, crystallisation at once occurred. The compound was now purified by repeated crystal-

# 1152 RÂY AND GUHA : MERCURY MERCAPTIDE NITRITES AND

lisation from methyl alcohol, and when pure it melted sharply at 93°. It consisted of the disulphonium compound,



0.2020 gave 0.1418  $\text{CO}_2$  and 0.0332  $\text{H}_2\text{O}$ .  $\text{C}=19.14$ ;  $\text{H}=1.82$ .

0.2055 „ 0.0507  $\text{Hg}$  „ 0.1750  $\text{AgI}$ .  $\text{Hg}=24.67$ ;  $\text{I}=46.02$ .

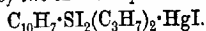
$\text{C}_{12}\text{H}_{13}\text{I}_3\text{S}_2\text{Hg}$  requires  $\text{C}=17.95$ ;  $\text{H}=1.52$ ;  $\text{Hg}=24.93$ ;

$\text{I}=47.51$  per cent.

As was to be expected, an interchange of radicle takes place in this case.

*Interaction of the Compound  $(\text{C}_{10}\text{H}_7)_2\text{S}_3\text{Hg}$  and Propyl Iodide:*

*Formation of the Monosulphonium Compound,*



From methyl-alcoholic solution the compound was deposited as an oil which, when kept in a vacuum for a week, solidified. It was then further purified by recrystallisation from methyl alcohol, when it melted at 106°:

0.1345 gave 0.1173  $\text{CO}_2$  and 0.0334  $\text{H}_2\text{O}$ .  $\text{C}=23.82$ ;  $\text{H}=2.76$ .

0.3701 „ 0.0900  $\text{Hg}$  „ 0.3101  $\text{HgI}$ .  $\text{Hg}=24.32$ ;  $\text{I}=45.28$ .

$\text{C}_{10}\text{H}_{21}\text{I}_3\text{SHg}$  requires  $\text{C}=23.25$ ;  $\text{H}=2.54$ ;  $\text{Hg}=24.21$ ;

$\text{I}=46.13$  per cent.

*Mercuric Nitrite and p-Tolyl Mercaptan: Formation of the Compound  $\text{C}_7\text{H}_7\cdot\text{S}(\text{hg})\cdot\text{S}(\text{HgNO}_2)\cdot\text{C}_7\text{H}_7$ .*

On adding an alcoholic solution of the mercaptan to the mercuric nitrite solution a product is obtained which on allowing to remain and occasionally stirring forms a dull yellow, granular mass. This is purified by crystallisation from hot benzene. Three successive crops melted at 127°. The purity of the compound is thus unquestionable. It evolves nitrous fumes when treated with hydrochloric acid:

0.0937 gave 0.0982  $\text{CO}_2$  and 0.0234  $\text{H}_2\text{O}$ .  $\text{C}=28.58$ ;  $\text{H}=2.77$ .

0.1419 „ 3.2 c.c.  $\text{N}_2$  at 25° and 760 mm.  $\text{N}=2.43$ .

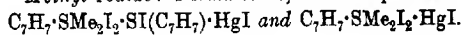
0.1316 „ 0.0737  $\text{HgS}$ .  $\text{Hg}=48.27$ .

$\text{C}_{28}\text{H}_{28}\text{O}_4\text{N}_2\text{S}_4\text{Hg}_3$  requires  $\text{C}=28.38$ ;  $\text{H}=2.36$ ;  $\text{N}=2.36$ ;

$\text{Hg}=50.68$  per cent.

*Interaction of the Mercaptide Nitrite of p-Tolyl Mercaptan and*

*Methyl Iodide: Formation of the Compounds*



A clear solution was obtained in this case on digesting the mercaptide nitrite with methyl iodide for three or four minutes. After

evaporating the excess of methyl iodide the oily residue was dissolved in acetone and the solution filtered. On concentrating and cooling, a small quantity of yellowish-white, scaly crystals began to be deposited. The compound was collected and washed with a small quantity of cold acetone. On recrystallising from hot methyl alcohol it melted sharply at  $109^{\circ}$ . The filtrate on evaporation of the acetone, left an oily residue, which was dissolved in methyl alcohol. On slow evaporation of the solvent, needle-shaped, yellow crystals melting at  $121^{\circ}$  were obtained.

The *disulphonium* compound melting at  $109^{\circ}$  gave the following results on analysis:

0.1656 gave 0.1215  $\text{CO}_2$  and 0.0428  $\text{H}_2\text{O}$ . C=20.08; H=2.87.

0.3418 „ 0.0735 Hg „ 0.2950 AgI. Hg=21.50; I=46.63.

$\text{C}_{16}\text{H}_{20}\text{I}_4\text{S}_2\text{Hg}$  requires C=19.51; H=2.03; Hg=20.32;  
I=51.63 per cent.

The *monosulphonium* compound melting at  $121^{\circ}$  gave the following results:

0.2718 gave 0.1440  $\text{CO}_2$  and 0.0686  $\text{H}_2\text{O}$ . C=14.45; H=2.80.

0.4152 „ 0.1132 Hg „ 0.3912 AgI. Hg=27.27; I=50.91.

$\text{C}_9\text{H}_{13}\text{I}_3\text{SHg}$  requires C=14.51; H=1.75; Hg=27.25;  
I=51.90 per cent.

*Interaction of the Mercaptide Nitrite of p-Tolyl Mercaptan and Ethyl Iodide: Formation of the Compounds*

$\text{C}_6\text{H}_7\cdot\text{SEt}_2\text{I}_2\cdot\text{SI}(\text{C}_7\text{H}_7)_2\cdot\text{HgI}$  and  $\text{C}_2\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{SEt}_2\text{I}_2\cdot\text{HgI}$ .

The method of procedure was exactly the same as described above. The *disulphonium* compound melts at  $120^{\circ}$ :

0.1235 gave 0.0240 Hg and 0.1111 AgI. Hg=19.43; I=48.63.

$\text{C}_{18}\text{H}_{24}\text{I}_4\text{S}_2\text{Hg}$  requires Hg=19.76; I=50.20 per cent.

The *monosulphonium* compound melts at  $70^{\circ}$ :

0.1387 gave 0.0946  $\text{CO}_2$  and 0.0320  $\text{H}_2\text{O}$ . C=18.60; H=2.54.

0.2943 „ 0.0746 Hg „ 0.2641 AgI. Hg=25.70; I=48.50.

$\text{C}_{12}\text{H}_{19}\text{I}_3\text{SHg}$  requires C=18.50; H=2.44; Hg=25.77;  
I=49.09 per cent.

*Interaction of the Mercaptide Nitrite of p-Tolyl Mercaptan and Propyl Iodide: Formation of the Monosulphonium Compound,*

$\text{C}_7\text{H}_7\cdot\text{SI}_2(\text{C}_3\text{H}_7)_2\cdot\text{HgI}$ .

In this case also (compare p. 1151) the compound could not be brought into the solid condition until it had been kept in a vacuum

desiccator for some days. Finally, it was crystallised from methyl alcohol, when it melted at  $71^{\circ}$ :

0.1670 gave 0.1193  $\text{CO}_2$  and 0.0425  $\text{H}_2\text{O}$ .  $\text{C}=19.48$ ;  $\text{H}=2.83$ .

0.3006 „ 0.0764  $\text{Hg}$  and 0.2520  $\text{AgI}$ .  $\text{Hg}=25.42$ ;  $\text{I}=46.30$ .

$\text{C}_{18}\text{H}_{21}\text{I}_3\text{SHg}$  requires  $\text{C}=19.75$ ;  $\text{H}=2.66$ ;  $\text{Hg}=25.32$ ;

$\text{I}=48.23$  per cent.

*Interaction of p-Chlorophenyl Mercaptan and Mercuric Nitrite:  
Formation of the Compound  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{S}(\text{hg})\cdot\text{S}(\text{HgNO}_2)\cdot\text{C}_6\text{H}_4\text{Cl}$ .*

This compound was crystallised from boiling benzene solution:

0.3576 gave 0.1662  $\text{Hg}$  and 0.1600  $\text{AgCl}$ .  $\text{Hg}=46.47$ ;  $\text{Cl}=11.07$ .

$\text{C}_{24}\text{H}_{16}\text{O}_4\text{N}_2\text{Cl}_4\text{Hg}_3$  requires  $\text{Hg}=47.39$ ;  $\text{Cl}=11.22$  per cent.

*Interaction of the Mercaptide Nitrite of p-Chlorophenyl Mercaptan  
and Methyl Iodide: Formation of the Compound  
 $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SMe}_3\text{I}_2\cdot\text{HgI}$ .*

This crystallised from hot methyl alcohol in yellow needles melting at  $129^{\circ}$ :

0.2647 gave 0.1202  $\text{CO}_2$  and 0.0400  $\text{H}_2\text{O}$ .  $\text{C}=12.38$ ;  $\text{H}=1.68$ .

0.3591 „ 0.0945  $\text{Hg}$ , 0.4118  $\text{AgI} + \text{AgCl}$ , and 0.2863  $\text{AgCl}$  by chlorination.  $\text{Hg}=26.32$ ;  $\text{I}=48.47$ ;  $\text{Cl}=6.19$ .

$\text{C}_8\text{H}_{10}\text{ClI}_3\text{SHg}$  requires  $\text{C}=12.73$ ;  $\text{H}=1.33$ ;  $\text{Hg}=26.51$ ;

$\text{I}=50.49$ ;  $\text{Cl}=4.70$  per cent.

The corresponding *ethyl* compound was at first deposited as an oil, but, when purified by repeated crystallisation, formed a yellow powder melting at  $64^{\circ}$ :

0.2796 gave 0.1446  $\text{CO}_2$  and 0.0495  $\text{H}_2\text{O}$ .  $\text{C}=14.11$ ;  $\text{H}=1.77$ .

0.4310 „ 0.1100  $\text{Hg}$ , 0.4506  $\text{AgI} + \text{AgCl}$ , and 0.3051  $\text{AgCl}$  by chlorination.  $\text{Hg}=25.52$ ;  $\text{I}=46.83$ ;  $\text{Cl}=4.42$ .

$\text{C}_{10}\text{H}_{14}\text{ClI}_3\text{SHg}$  requires  $\text{C}=15.34$ ;  $\text{H}=1.79$ ;  $\text{Hg}=25.57$ ;

$\text{I}=48.71$ ;  $\text{Cl}=4.54$  per cent.

*Reaction of Ethyl Sulphide and Mercuric Iodide with Alkyl Iodides.*

A mixture of ethyl sulphide and ethyl iodide was heated under reflux with an excess of mercuric iodide, when a golden-yellow liquid was obtained. It was dissolved in a minimum quantity of acetone and precipitated by ether and the process repeated. A yellow, crystalline powder was obtained, which melted at  $110^{\circ}$ . A small quantity remained insoluble in acetone and melted at  $146\text{--}147^{\circ}$  (com-

are Part VI). The compound melting at  $110^{\circ}$  gave the following results:

0.1984 gave 0.0757  $\text{CO}_2$  and 0.0427  $\text{H}_2\text{O}$ .  $\text{C}=10.41$ ;  $\text{H}=2.39$ .  
 0.2775 „ 0.0764  $\text{Hg}$  „ 0.2708  $\text{AgI}$ .  $\text{Hg}=27.53$ ;  $\text{I}=52.74$ .

$\text{C}_6\text{H}_{15}\text{I}_3\text{SHg}$  requires  $\text{C}=10.29$ ;  $\text{H}=2.14$ ;  $\text{Hg}=28.57$ ;  
 $\text{I}=54.43$  per cent.

A mixture of ethyl sulphide and methyl iodide was treated with excess of mercuric iodide as above. The yellow, crystalline product melted at  $65-67^{\circ}$ :

0.2652 gave 0.0862  $\text{CO}_2$  and 0.052  $\text{H}_2\text{O}$ .  $\text{C}=8.86$ ;  $\text{H}=2.180$ .  
 0.5618 „ 0.1595  $\text{Hg}$  „ 0.5347  $\text{AgI}$  and 0.1480  $\text{BaSO}_4$ .  $\text{Hg}=28.91$ ;  $\text{I}=52.36$ ;  $\text{S}=3.68$ .

$\text{C}_5\text{H}_{13}\text{I}_3\text{SHg}$  requires  $\text{C}=8.75$ ;  $\text{H}=1.90$ ;  $\text{Hg}=29.15$ ;  $\text{I}=55.53$ ;  
 $\text{S}=4.67$  per cent.

The corresponding yellow, crystalline *propyl* derivative melted  $88-89^{\circ}$ :

0.1904 gave 0.0861  $\text{CO}_2$  and 0.0480  $\text{H}_2\text{O}$ .  $\text{C}=12.33$ ;  $\text{H}=2.81$ .  
 0.3796 „ 0.1038  $\text{Hg}$  „ 0.3569  $\text{AgI}$ .  $\text{Hg}=27.35$ ;  $\text{I}=50.83$ .

$\text{C}_7\text{H}_{17}\text{I}_3\text{SHg}$  requires  $\text{C}=11.77$ ;  $\text{H}=2.38$ ;  $\text{Hg}=28.00$ ;  
 $\text{I}=53.36$  per cent.

The corresponding yellow, crystalline *butyl* derivative melted at  $71-73^{\circ}$ :

0.3829 gave 0.1874  $\text{CO}_2$  and 0.0673  $\text{H}_2\text{O}$ .  $\text{C}=13.35$ ;  $\text{H}=1.95$ .  
 0.5745 „ 0.1565  $\text{Hg}$ .  $\text{Hg}=27.24$ .

$\text{C}_8\text{H}_{19}\text{I}_3\text{SHg}$  requires  $\text{C}=13.19$ ;  $\text{H}=2.61$ ;  $\text{Hg}=27.47$  per cent.

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[Received, May 12th, 1919.]

## II.—*Asymmetric Replacement in the meta-Series.* *Part I.*

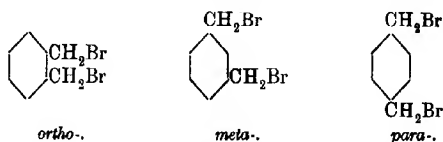
By WILLIAM HENRY GOUGH and JOCELYN FIELD THORPE.

THE interaction of organic halogen derivatives containing two atoms of the halogen and substances of the type of potassium cyanide usually leads to the replacement of both halogen atoms and the subsequent production of the corresponding dinitriles. If an sufficient quantity of potassium cyanide is present completely to effect this change, it generally happens that the whole of the cyanide is utilised in forming the dinitriles and the rest of the

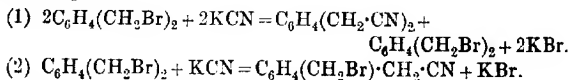


dihalogen derivatives remains unaltered. This is, at any rate, the usual course of the reaction when the halogen atoms are symmetrically placed in the organic molecule, although it is obvious that asymmetric substitution, that is, the successive replacement of the halogen atoms, with the intermediate formation of the compound in which only one halogen atom is substituted, can and does take place when the halogen atoms are in positions in the organic molecule which cause them to possess different degrees of reactivity, and therefore render one of them more open to attack than the other.

There is thus no reason to suppose that the three  $\omega\omega'$ -dibromoxylenes (xylene dibromides), in each of which the bromine atoms



are symmetrically placed to each other, would exhibit any fundamental differences in their behaviour towards alcoholic potassium cyanide under the same experimental conditions, and yet the evidence brought forward in this communication shows clearly that whereas the *o*- and *p*-compounds are converted directly into the dinitriles without any intermediate formation of the bromonitriles,  $C_6H_4(CH_2Br) \cdot CH_2 \cdot CN$ —even though an insufficient quantity of potassium cyanide to form the dinitrile is present—the bromine atoms in the meta-compound can be easily replaced successively, and that it is a simple matter to prepare the *m*-bromo-nitrile, of the above formula, in considerable quantities. In other words, the reaction between  $\omega\omega'$ -dibromo-*o*-(or *p*-)xylene and alcoholic potassium cyanide (equal molecules) is represented by equation (1), whereas equation (2) represents the reaction in the case of the meta-compound:



It is certainly remarkable that this property of the meta-compound should have been hitherto unrecognised, because the conversion of all three  $\omega\omega'$ -dibromoxylenes into the nitriles has been carried out by several investigators. Indeed, it was while we were attempting to prepare the *m*-dinitrile by what we understood to be Kipping's method that the isolation of this intermediate product occurred. It happens that the reference to Kipping's paper is quoted wrongly in "Beilstein," and the details of the preparation given there, which are evidently taken from the paper by Oddo

(*Gazzetta*, 1893, **23**, ii, 338), state that twenty hours on the water-bath are sufficient to convert 13.4 grams of  $\omega\omega'$ -dibromo-*m*-xylene, 9 grams of potassium cyanide, and 500 c.c. of alcohol completely into the dinitrile and potassium bromide. As a matter of fact, in our hands these conditions led to a 90 per cent. yield of the pure *m*-bromo-nitrile, and we were unable to isolate any trace of the dinitrile. A subsequent reference to Kipping's paper (T., 1888, **53**, 41) showed that he had heated his reaction mixture on the water-bath for a "considerable time." It is certain, moreover, that Kipping's product could not have contained any appreciable quantity of the bromo-nitrile, because he found that the crude oil formed in his reaction gave an almost theoretical yield of *m*-phenylenediacetic acid when it was hydrolysed by alcoholic potassium hydroxide (*ibid.*, p. 43).

It seemed therefore desirable to carry out a series of comparative experiments on the behaviour of the three  $\omega\omega'$ -dibromoxylenes towards potassium cyanide under different conditions in order to ascertain whether this property of asymmetric replacement was characteristic of the meta-series, and whether, in fact, we had to hand another example of abnormal behaviour in these derivatives.

$\omega\omega'$ -Dibromo-*o*-xylene has been converted into the dinitrile by Baeyer and Pape (*Ber.*, 1884, **17**, 447); similar conditions were subsequently employed by Moore and Thorpe (T., 1908, **93**, 175) for the preparation of large quantities of the compound. When 10 per cent. more than the amount of potassium cyanide, representing two molecular proportions, is used and the quantity of the solvent is reduced to a minimum, the reaction proceeds smoothly and is finished at the end of an hour, the heat generated being sufficient to carry the change to completion.

The yield is good, and the only by-product accompanying the dinitrile is a small quantity of oily impurity of indefinite character; no trace of the bromo-nitrile can be detected.

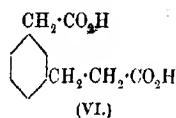
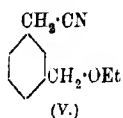
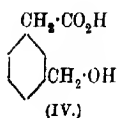
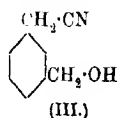
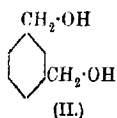
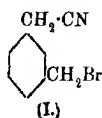
The interaction of one molecular proportion of  $\omega\omega'$ -dibromo-*o*-xylene and one of potassium cyanide was investigated by Moore and Thorpe during the earlier experiments (*loc. cit.*), but the details were not then published, because the preparation of the intermediate bromo-nitrile, which was the object in view, was not achieved. A description of this work is now included in the experimental portion of this paper; it shows clearly that the reaction proceeds in accordance with equation (1) above.

*p*-Phenylenediacetonitrile has been prepared by Klippert (*Ber.*, 1876, **9**, 1766) from  $\omega\omega'$ -dichloro-*p*-xylene, and by Kipping (T., 1888, **53**, 44) from the corresponding dibromo-derivative. Kipping found that the yield of the dinitrile was only approximately 50 per

cent. of the theoretical, the remainder of the product being an amorphous substance of resinous character; we agree with him that it does not appear possible to avoid the formation of this resin or to increase the yield of the dinitrile by varying the conditions. The reaction under his conditions proceeds smoothly, but requires a longer time than is the case with the ortho-derivative; no trace of the bromo-nitrile is formed.

When one molecular proportion of  $\omega\omega'$ -dibromo-*p*-xylene and one of potassium cyanide are employed, the reaction proceeds in accordance with equation (1), approximately 50 per cent. of the dibromo-compound being recovered unchanged and the remainder being converted into the dinitrile.

The references in connexion with the preparation of *m*-phenylenediacetonitrile have already been given, and we have stated that, in our hands, the published experimental conditions led to the formation of the *m*-bromo-nitrile (I) as sole product. The constitution of this substance has been placed beyond question by its conversion into the already known  $\omega\omega'$ -dihydroxy-*m*-xylene (II) (Colson, *Ann. Chim. Phys.*, 1885, [vi], 6, 112) by the action of freshly precipitated silver hydroxide. We have also further characterised it by the formation of the hydroxy-nitrile (III), the hydroxy-acid (IV), the ethoxy-derivative (V), and the acid (VI) which is formed by condensing it with the sodium compound of ethyl malonate and hydrolysing the product. Experiments were also carried out in order



to ascertain whether the state of dilution of the potassium cyanide had any influence on the course of the reaction in the three series, but this was found not to be the case, and it is evident, therefore, that the property of asymmetric replacement in a compound possessing apparent symmetry is characteristic of the meta-series.

## EXPERIMENTAL.

*The Interaction of Alcoholic Potassium Cyanide (1 mol.) and  $\omega\omega'$ -Dibromo-*o*-(and *p*-)xylene (1 mol.).*

*$\omega\omega'$ -Dibromo-*o*-xylene.*—This operation was carried out in a manner similar to that described in the earlier paper (Moore and Thorpe, T., 1908, **93**, 175), but care was taken to keep, as far as possible, to the theoretical amounts required by equation (1) (p. 1156).

Fifty-three grams of pure  $\omega\omega'$ -dibromo-*o*-xylene melting at  $95^{\circ}$ , and in a finely ground condition, were added gradually to a boiling solution containing 13 grams of Kahlbaum's purest potassium cyanide, which had been prepared by dissolving the cyanide in the smallest possible amount of cold water and adding three times the volume of absolute alcohol. When all the dibromide had been added, the mixture was allowed to remain for half an hour, when it was diluted with water, and the oil, which was then precipitated, extracted with ether. The dried ethereal solution was freed from the solvent, and the oily residue submitted to careful fractionation under diminished pressure (20 mm.). The fraction boiling below  $160^{\circ}$  was then redistilled, and the portion boiling between  $135^{\circ}$  and  $140^{\circ}$  collected. The distillate solidified, and was found to melt, without further purification, at  $94-95^{\circ}$ . An analysis (Found: Br = 60.71.  $C_8H_6Br_2$  requires Br = 60.6 per cent.) proved it to be pure  $\omega\omega'$ -dibromo-*o*-xylene. The amount recovered weighed 24.7 grams, or, in other words, it represented approximately 50 per cent. of the dibromo-compound originally used.

*$\omega\omega'$ -Dibromo-*p*-xylene.*—In this case, the same conditions and quantities as those given above were used, excepting that, after all the dibromide had been added, the mixture was heated on the water-bath for four hours. Fractionation of the oily product gave a quantity of distillate boiling below  $160^{\circ}/20$  mm., and this on redistillation gave 25 grams of liquid boiling at  $145^{\circ}/21$  mm., which rapidly solidified in the receiver. The solid melted, without further purification, at  $143^{\circ}$ , and an analysis (Found: Br = 60.56.  $C_8H_6Br_2$  requires Br = 60.6 per cent.) proved it to be pure  $\omega\omega'$ -dibromo-*p*-xylene. In this case also it is evident that the reaction had proceeded in accordance with equation (1) (p. 1156), and that approximately 50 per cent. of the dibromo-compound had been recovered unchanged.

The residue left in the flask after the  $\omega\omega'$ -dibromo-*o*-xylene had been distilled off, together with a small quantity obtained on subsequently refractionating the distillate, solidified on cooling, and

when recrystallised from alcohol yielded 14.5 grams of pure *o*-phenylenediacetonitrile melting at 60°. On the other hand, the residues from the  $\omega\omega'$ -dibromo-*p*-xylene experiment, which also solidified on cooling, gave only 8 grams of the dinitrile melting at 98° when recrystallised.

*The Interaction of  $\omega\omega'$ -Dibromo-*m*-xylene and Alcoholic Potassium Cyanide under Different Conditions.*

- (1) *Experiments involving the Use of  $\omega\omega'$ -Dibromo-*m*-xylene\* (1 mol.) and Potassium Cyanide (2 mols.). (a) Oddo's Method (loc. cit.).*

$\omega\omega'$ -Dibromo-*m*-xylene (13.4 grams) and 9 grams of potassium cyanide (pure and finely ground) were mixed with 500 c.c. of alcohol and heated in a flask fitted with a reflux condenser for twenty hours on the water-bath. The alcohol was then distilled off and water added, the precipitated oil and aqueous liquid being extracted by ether. The washed and dried ethereal solution yielded an oil on evaporating the solvent, which, when distilled under 18 mm. pressure, gave 9.5 grams of a colourless oil boiling at 140–141°. This oil appeared to be the sole product of the reaction.

(b) The quantities and conditions employed in this case were based on those used by Atkinson and Thorpe (T., 1907, 91, 1699) for the production of the three tolylacetonitriles. Sixty grams of pure, finely ground potassium cyanide were dissolved in the smallest possible quantity of water, and then diluted to 500 c.c. with alcohol. To this solution were added 50 grams of recrystallised  $\omega\omega'$ -dibromo-*m*-xylene dissolved in 200 c.c. of alcohol. The whole was then heated on the water-bath under a reflux condenser for twenty-four hours, when it was noticed that, after the reaction had been in progress for two hours, an orange-coloured precipitate formed, the amount of which continued to increase for some time. At the end of the time specified, the alcohol was removed by distillation, water added in sufficient quantity to dissolve the potassium salts, and the mixture, after being cooled to 0°, filtered. The precipitate was then washed with hot alcohol, in which the nitrile is readily soluble, and the oil recovered from the alcohol in the usual way. It boiled at 140–141°/18 mm., and weighed 36 grams; there was no fraction of higher boiling point. The orange-coloured precipitate was purified by repeated extraction with hot alcohol and then with boiling water. It was an amorphous substance evidently of high molecular weight, since it did not melt and was insoluble in all the

\* In all the experiments described in this section pure  $\omega\omega'$ -dibromo-*m*-xylene melting at 76–77° was used.

usual organic solvents. An analysis showed it to contain N=10.4 per cent., but we have not as yet been able to assign any constitution to it. Its formation was evidently due to the large excess of potassium cyanide used in the reaction.

(c) Finally, an experiment was carried out in order to see whether the dilution of the potassium cyanide had any important influence on the nature of the product, the proportions used being the same as those given by Oddo. Thus, 53.6 grams of the dibromo-compound and 36 grams of potassium cyanide were taken, together with 500 c.c. of alcohol, that is, about one-fourth the quantity used by Oddo, the reaction being carried out in precisely the same way as described in experiment (a). Here again the sole product was a colourless oil boiling at 140–141°/18 mm., the weight obtained being 38 grams.

(2) *Experiment involving the Use of  $\omega\omega'$ -Dibromo-m-xylene (1 mol.) and Potassium Cyanide (1 mol.).*—The conditions used in this experiment were the same as those given in the case of  $\omega\omega'$ -dibromo-*o*-(and *p*-)xylene on p. 1159, the mixture being, however, heated for ten hours on the water-bath before being worked up. In this case, the whole of the liquid product boiled at 140–141°/18 mm., that is, at practically the same temperature as the dibromo-compound used. An analysis showed, however, that it was the pure bromo-nitrile (Found: Br=38.12.  $C_8H_5Br_2$  requires Br=60.6;  $C_8H_5NBr$  requires Br=38.1 per cent.). The yield was almost theoretical.

*$\omega$ -Bromo-m-tolylacetanitrile* (I. p. 1158).

This substance, prepared by any of the methods described above, is a colourless, mobile liquid which, as already stated, boils at 140–141°/18 mm., or, with slight decomposition, at 220–221°/756 mm. The yield is approximately 90 per cent. of that theoretically possible:

0.0863 gave 0.1625  $CO_2$  and 0.0313  $H_2O$ . C=51.45; H=4.05.

0.2099 (by Carius' method) gave 0.1879 AgBr. Br=38.10.

0.4865 (by alcoholic  $AgNO_3$ ) required 0.3698  $AgNO_3$ . Br=37.99.

$C_9H_9NBr$  requires C=51.4; H=3.8; Br=38.1 per cent.

An attempt to determine the nitrogen content failed, owing to the fact that the substance reacted with copper oxide at the ordinary temperature, and the combustion was therefore practically complete before the air had been swept from the tube. An estimation was carried out by Kjeldahl's method, but here again no accurate result was obtained, due doubtless to the destruction of part of the ammonia by the bromine liberated. The bromo-nitrile is in many

ways a curious compound, and is very inert towards most of the usual reagents. For example, it is not acted on by concentrated hydrochloric acid even after prolonged boiling, and is unaffected by 64 per cent. aqueous potassium hydroxide or by mild reducing agents. On the other hand, it gives a characteristic reaction with concentrated sulphuric acid, forming, even when only very small quantities are used, a deep reddish-brown solution which rapidly sets to a jelly. The action of water precipitates a yellow powder which, as the following analysis shows, possesses the same empirical formula as the original bromo-nitrile:

0.1563 gave 0.2940  $\text{CO}_2$  and 0.0549  $\text{H}_2\text{O}$ .  $\text{C}=51.3$ ;  $\text{H}=3.9$ .

0.2542 „ 0.2270  $\text{AgBr}$ .  $\text{Br}=38.0$ .

0.2136 „ 12 c.c.  $\text{N}_2$  at  $15^\circ$  and 765.8 mm.  $\text{N}=6.65$ .

$\text{C}_9\text{H}_8\text{NBr}$  requires  $\text{C}=51.4$ ;  $\text{H}=3.8$ ;  $\text{N}=6.7$ ;  $\text{Br}=38.1$  per cent.

The structure of this substance is under investigation.

*ωω'*-Dihydroxy-*m*-xylene (II, p. 1158) and *ω*-Hydroxy-*m*-tolyl-acetonitrile (III, p. 1158).

The bromo-nitrile is readily converted into a mixture of these two substances when it is treated for half an hour with an excess of freshly precipitated silver hydroxide. The oil, which can be extracted from the product, after filtration, by ether, can be readily separated into two fractions, one boiling at  $154\text{--}159^\circ/13$  mm., and another boiling at  $145^\circ$  under the same pressure. The former solidifies on keeping and melts at  $47^\circ$  (Found:  $\text{C}=69.6$ ;  $\text{H}=7.2$ .  $\text{C}_8\text{H}_{10}\text{O}_2$  requires  $\text{C}=69.5$ ;  $\text{H}=7.2$  per cent.). Since it readily gives isophthalic acid on oxidation, it is evidently *ωω'*-dihydroxy-*m*-xylene, originally prepared by Colson (*loc. cit.*). The fraction of lower boiling point ( $145^\circ/13$  mm.) was analysed:

0.1403 gave 0.3770  $\text{CO}_2$  and 0.0770  $\text{H}_2\text{O}$ .  $\text{C}=73.3$ ;  $\text{H}=6.1$ .

0.1346 „ 10.95 c.c.  $\text{N}_2$  at  $16^\circ$  and 762.3 mm.  $\text{N}=9.54$ .

$\text{C}_9\text{H}_9\text{ON}$  requires  $\text{C}=73.5$ ;  $\text{H}=6.1$ ;  $\text{N}=9.5$  per cent.

It is evidently *ω*-hydroxy-*m*-tolylacetonitrile, since it yields *ω*-hydroxy-*m*-tolylacetic acid (see below) on treatment with hydrochloric acid. The hydroxy-nitrile is a colourless, pleasant-smelling oil which decomposes when distilled under the ordinary pressure. Although their boiling points lie so close together, the separation of these two compounds by fractional distillation is complete.

*ω*-Hydroxy-*m*-tolylacetic Acid (IV, p. 1158).

This acid can be prepared from the above hydroxy-nitrile by boiling it with concentrated hydrochloric acid, and from the bromo-

nitrile by treatment with aqueous sulphuric acid (1:1) in a sealed tube for six hours at 150°. The acid is extracted by ether, and it is advisable to neutralise the residue, left after evaporating the ether, with dilute ammonia, and again to extract with ether, in order to remove non-acidic impurities, before finally precipitating the acid by means of hydrochloric acid. It crystallises from dilute hydrochloric acid in white, glistening plates melting at 128°:

0.1532 gave 0.3656 CO<sub>2</sub> and 0.0835 H<sub>2</sub>O. C=65.0; H=6.05.

C<sub>9</sub>H<sub>10</sub>O<sub>3</sub> requires C=65.1; H=6.0 per cent.

The acid is freely soluble in alcohol, ether, or hot water.

*ω-Ethoxy-m-tolylacetoneitrile* (V, p. 1158).

The bromo-nitrile (10.5 grams) is converted into this ethoxy-derivative when it is treated with an alcoholic solution of sodium ethoxide—prepared by dissolving 1.2 grams of sodium in 30 c.c. of alcohol—in the first instance at the ordinary temperature for eight hours, and finally on the water-bath for one hour. Water is then added and the oil extracted by ether, the dried ethereal solution leaving a residue on evaporation which, on distillation, yields the ethoxy-derivative as a colourless, mobile oil boiling at 161–162°/13 mm.:

0.1020 gave 0.2790 CO<sub>2</sub> and 0.0712 H<sub>2</sub>O. C=74.59; H=7.6.

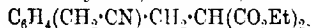
0.1285 „ 8.60 c.c. N<sub>2</sub> at 14° and 768.1 mm. N=7.99.

C<sub>11</sub>H<sub>13</sub>ON requires C=75.4; H=7.4; N=8.0 per cent.

It is a remarkable fact that although the above Dumas estimation gave results in accordance with theory, and that the odour of ammonia could be detected when the compound was hydrolysed by alkali, several very careful tests by the metallic sodium method failed to reveal a trace of nitrogen.

*The Condensation of Ethyl Sodiomalonate with ω-Bromo-m-tolyl-acetonitrile.*

*Ethyl ω-Cyano-m-methylbenzylmalonate,*



—This substance is formed by allowing a solution containing 16 grams of ethyl malonate, which has been converted into its sodium derivative by means of 1.2 grams of sodium dissolved in 30 grams of alcohol, to react with 10.5 grams of the bromo-nitrile at the temperature of the water-bath for four to five hours. It is precipitated as an oil on the addition of water, and can be extracted with ether and isolated in the usual way. The ester boils at 201–203°/18 mm.:



0.1266 gave 0.3082  $\text{CO}_2$  and 0.0754  $\text{H}_2\text{O}$ .  $\text{C}=66.39$ ;  $\text{H}=6.62$ .

0.3012 „ 12.9 c.c.  $\text{N}_2$  at  $17^\circ$  and 764.4 mm.  $\text{N}=4.9$ .

$\text{C}_{16}\text{H}_{19}\text{O}_4\text{N}$  requires  $\text{C}=66.4$ ;  $\text{H}=6.6$ ;  $\text{N}=4.8$  per cent.

The ester is quickly hydrolysed, by a solution containing rather more than the calculated quantity of sodium hydroxide, at a gentle heat, and the acid,  $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{CN})\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ , is formed as a crystalline precipitate when the solution is acidified. It was not found possible, however, to recrystallise this acid, because when its solutions in solvents are heated, carbon dioxide is quickly eliminated. If, for example, its aqueous solution is boiled,  *$\beta$ - $\omega$ -cyano-m-tolylpropionic acid*,  $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{CN})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , separates on cooling. This acid crystallises from water, containing a little hydrochloric acid, in white, glistening plates melting at  $148^\circ$ , and closely resembling anthracene in appearance:

0.1124 gave 0.2878  $\text{CO}_2$  and 0.0590  $\text{H}_2\text{O}$ .  $\text{C}=69.79$ ;  $\text{H}=5.90$ .

0.1758 „ 11.5 c.c.  $\text{N}_2$  at  $20^\circ$  and 757.9 mm.  $\text{N}=7.41$ .

$\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$  requires  $\text{C}=69.8$ ;  $\text{H}=5.8$ ;  $\text{N}=7.4$  per cent.

*$\beta$ - $\omega$ -Carbonyl-m-tolylpropionic Acid* (VI, p. 1158).

This acid is best prepared from the cyano-acid described above by dissolving it in three times its weight of concentrated sulphuric acid, allowing the solution to remain for two hours, and then, after diluting it with three times its volume of water, boiling for three hours. The acid is then collected and washed with ether, being finally recrystallised from dilute alcohol, when it is obtained in fine needles which melt at  $132^\circ$ :

0.1045 gave 0.2431  $\text{CO}_2$  and 0.0543  $\text{H}_2\text{O}$ .  $\text{C}=63.40$ ;  $\text{H}=5.82$ .

$\text{C}_{11}\text{H}_{13}\text{O}_4$  requires  $\text{C}=63.5$ ;  $\text{H}=5.8$  per cent.

The acid is sparingly soluble in hot water or ether, but readily so in alcohol. The *calcium* salt is insoluble in hot water, and the *potassium* salt crystallises from water in plates.

This work was carried out during the tenure by one of us (W.H.G.) of a fellowship granted by the Salters' Company.

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SOUTH KENSINGTON. [Received, September 3rd, 1918.]

CIV.—*Molecular-weight Determination by Direct Measurement of the Lowering of the Vapour Pressure of Solutions.*

By ROBERT WRIGHT.

THE direct measurement of the vapour pressure of solutions has never been very extensively used as a means of determining molecular weights. The barometric method as originally employed by Raoult is too cumbersome for general use, and at the ordinary temperature the lowerings of the vapour pressure obtained with most solvents are too small to admit of accurate measurement by this means. A simple method for use with a volatile liquid, such as ether, was described in a former paper (P., 1912, 28, 96), but it is quite unsuitable in the case of the more common solvents.

Menzies (*J. Amer. Chem. Soc.*, 1910, 32, 1615) has described an apparatus in which the lowering of the vapour pressure produced by a solute is measured at the boiling point of the solution, the manometric liquid used being the solution itself; so that, both on account of the high temperature of the determination and the sensitiveness of the manometer, very dilute solutions can be employed in the measurements.

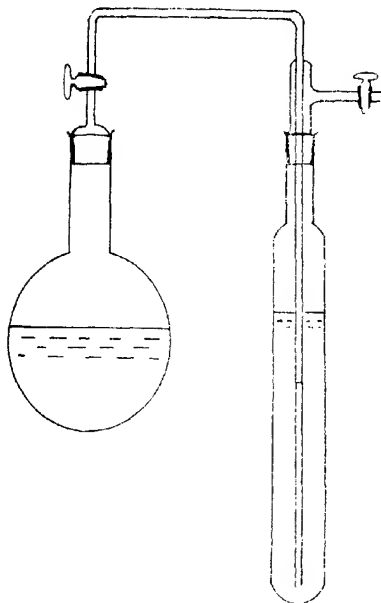
The apparatus about to be described resembles that of Menzies in that the solution is used as the manometric liquid, but all measurements are carried out at the ordinary temperature, and as the apparatus is of simple design, it can readily be constructed of ordinary laboratory material. A flask, or bottle, of 150 c.c. capacity is fitted with a ground-in delivery tube which carries a well-fitting tap placed just above the flask, the other end of the delivery tube passing almost to the bottom of a test-tube about 20 cm. long and 2—3 cm. wide. The neck of the test-tube is fitted with a hollow stopper, through which the delivery tube is sealed; the stopper also carries a side-tube fitted with a tap. It will be seen that the test-tube is of the same construction as an ordinary Drechsel gas-washing bottle fitted with a stop-cock; in fact, the first piece of apparatus employed consisted of such a wash-bottle; it was, however, abandoned, on account of the large amount of solution required, and the smaller test-tube substituted.

In carrying out a determination, a weighed quantity of the solute is placed in the test-tube, and after both flask and tube have been half filled with solvent, the apparatus is connected together,

X X\*

all ground connexions being carefully treated with rubber grease. The apparatus is now exhausted by means of a filter-pump so that all air is boiled out of both solvent and solution; to assist this boiling-out process, the flask containing the solvent may be heated gently, either with the hand or by means of a beaker of warm water; it is also advisable to sweep out the air in gusts by alternately closing and opening the tap between the flask and test-tube.

When exhaustion is complete, a process which should occupy



about half an hour, both taps are closed and the apparatus is left to itself for two or three hours to attain the ordinary temperature. The tap between the flask and test-tube should be closed during this period to prevent the forcing back of the solution into the pure solvent as a result of accidental leakage of air into the test-tube. When the ordinary temperature has been reached, the tap above the flask is gently opened, and as the vapour pressure of the solvent exceeds that of the solution, the liquid in the delivery tube is depressed below the ordinary level of the liquid in the test-tube.

This difference in height is measured either by means of a cathetometer or by having the delivery tube graduated in mm.; in either case, the observed height must be corrected for capillarity. As a check on the manometer reading, it is usually advisable to re-exhaust the apparatus without warming the solvent flask, and as the solution in the test-tube will remain practically unchanged in volume, a second pressure-reading almost identical with the first should be obtained. The temperature of the room is noted at the same time as the manometer reading is taken, and air is then admitted to the apparatus by gently raising the tap above the flask out of its seat, care being taken to prevent a violent inrush of air; the effect of capillarity is now noted, after which the test-tube is removed and weighed, and the mass of the solution so determined. If the solution is a concentrated one, its density should also be measured; in the case of dilute solutions, the density may be considered as equal to that of the solvent.

The molecular weight of the solute is calculated from the usual formula for the lowering of the vapour pressure,

$$M = \frac{P'Sm}{(P - P')s},$$

where  $M$  and  $m$  are the molecular weights of the solute and solvent,  $S$  and  $s$  their weights in grams,  $P$  the vapour pressure of the pure solvent, and  $P'$  that of the solution. The vapour pressure of the pure solvent at the temperature of the experiment is obtained by consulting tables, interpolating, if necessary, on the assumption that the curve connecting the logarithm of the vapour pressure and the temperature is a straight line.

The results obtained with alcohol and carbon tetrachloride as solvents are shown in the following table:

*Alcohol as Solvent.*

| Solute             | $S$ . | $s$ . | $T$ . | $P$ . | $H$ . | $P - P'$ . | $M$ . | $M$ (true) |
|--------------------|-------|-------|-------|-------|-------|------------|-------|------------|
| Benzoic acid ..... | 5.698 | 78    | 19.5  | 42.6  | 17.8  | 1.084      | 128   | 122        |
| Carbamide .....    | 4.043 | 108   | 19.0  | 41.4  | 21.0  | 1.237      | 56    | 60         |
| Acetamide .....    | 3.781 | 102   | 17.0  | 36.6  | 17.5  | 1.029      | 59    | 59         |

*Carbon Tetrachloride as Solvent.*

|                   |       |    |      |      |      |       |     |     |
|-------------------|-------|----|------|------|------|-------|-----|-----|
| Naphthalene ..... | 0.784 | 48 | 15.5 | 73.3 | 13.0 | 1.517 | 118 | 128 |
| Phenanthrene ...  | 1.072 | 49 | 19.0 | 87.1 | 14.6 | 1.697 | 168 | 178 |

The headings of the different columns have the meanings ascribed to them in the formula. Column  $H$  gives the manometer readings in mm. of the solution, the heights being corrected for capillarity.

With regard to the solvents that may be employed, water is not

suitable, both on account of its very small vapour pressure and its low molecular weight. Alcohol and carbon tetrachloride were both satisfactory, although the latter showed some tendency to dissolve the rubber grease with which the taps were coated. The solvent action of the vapour on the tap lubricant quite prevented the use of benzene, and the plan of treating the taps with syrupy phosphoric acid instead of rubber proved unsuccessful, as the taps so lubricated seemed incapable of holding a vacuum.

A point of theoretical interest might be mentioned, as it applies both to the above method and that of Menzies. The vapour in the flask and delivery tube is confined between the pure solvent in the flask and the solution in the tube, and therefore it might be concluded that its pressure would lie between the values  $P$  and  $P'$ . Further consideration will show, however, that such a state is not in equilibrium, and that distillation will take place from the high pressure to the low, that is, from the solvent to the solution, until a layer of pure solvent is obtained lying on the top of the solution in the delivery tube, under which conditions the pressure of the vapour in the flask and delivery tube will be equal to that of the pure solvent.

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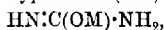
[Received, June 25th, 1919.]

CV.—*The Constitution of Carbamides. Part X.  
The Behaviour of Urea and of Thiourea towards  
Diazomethane and Diazoethane respectively.  
The Oxidation of Thiourea by Potassium Per-  
manganate.*

By EMIL ALPHONSE WERNER.

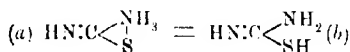
It was shown by Degner and von Pechmann (*Ber.*, 1897, **30**, 647) that urea is indifferent towards diazomethane dissolved in ether. In a recent communication (this vol., p. 1098), the author has drawn attention to the fact that the action of diazomethane as a methylating agent can be conveniently studied in alcoholic solution. It was considered desirable, therefore, to test the behaviour of urea under this condition, since the result of Degner and von Pechmann's experiment could not be reasonably accepted as final, on account of the insolubility of urea in ether.

It is now shown that even when diazomethane was generated in situ with urea dissolved in alcohol, which had been previously dried by means of diazomethane, the whole of the urea was recovered unchanged after it had remained for twenty-four hours in contact with the reagent. A similar result was obtained with diazoethane. This fact is in perfect agreement with the view that the cyclic form of the urea molecule alone obtains in a neutral solution. The reactive "amino-hydroxyl" configuration occurs only when a sufficiently strong acid or alkali is present, that is, under such conditions that a salt of the type  $\text{HN:C(OH)·NH}_2\text{·HX}$  or

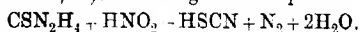


as the case may be, can exist in solution (T., 1918, 113, 86).

The case of thiourea is different. Its behaviour towards iodine, with the formation of formamidine disulphide (T., 1912, 101, 2175), the well-known reaction with alkyl haloids, whereby thioesters of the type  $\text{HN:C(SR)·NH}_2$  are produced, and particularly its reactions with nitrous acid (T., 1912, 101, 2180; 1913, 103, 1221), all go to prove that in a neutral solution thiourea must be present in two molecular forms in equilibrium, thus:

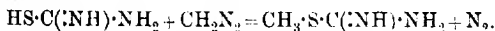


It may be well here to point out a fact which was not shown before (Expt. VI), namely, that, in contrast with urea (T., 1917, 111, 875), thiourea is rapidly decomposed by nitrous acid alone (at concentration  $N/30$ ), according to the equation



It is obvious that it is form (b) that is attacked by way of the aminogroup, since the sulphur remains in its original state of combination in the decomposition product, namely, thiocyanic acid.

Convincing evidence in support of the above view is supplied by the fact that thiourea is attacked by diazomethane in alcoholic solution, thus:



The so-called methylisothiurea\* was readily isolated in the form of its picrate, which melted at  $221^\circ$ . The reaction proceeded slowly at first, indicating the presence of form (b) in small amount; as the temperature gradually rose, the velocity of the change from (a) to (b) was rapidly promoted. Since the free base is unstable,

\* The term "isothiurea" is commonly used with reference to its relation to the "thiocarbamide" formula, the existence of which the author does not admit under any conditions. Thiourea is "isothiurea" in its reactive form in solution.

it was partly decomposed, with the production of methyl mercaptan, the odour of which was evident as soon as the reaction commenced.

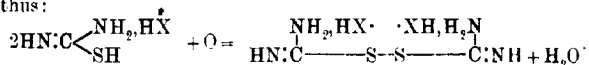
Ethylisothiouraea picrate, which melted at 188°, was isolated from the reaction product when diazoethane was used, the change having proceeded on lines similar to the above.

When thiourea was treated with two molecular proportions of diazomethane, the excess of the latter showed no tendency to attack the methylisothiouraea formed in the first instance, a result which, taken into consideration with the indifference of urea towards diazomethane, shows that an imino-group in the form  $\text{HN}:\text{C}:$  is not methylated by the reagent. In this connexion, it is interesting to note that the system  $\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot$  is capable of methylation; thus Pechmann (*Ber.*, 1895, **28**, 855) obtained methylphthalimide, and Nierenstein (*private communication*) methylsuccinimide, from their respective parent compounds.

*Oxidation of Thiourea by Potassium Permanganate.*

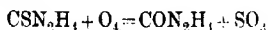
Interesting evidence in support of the existence of the two forms of thiourea in solution is supplied by a study of its oxidation by potassium permanganate under different conditions.

It was shown (T., 1912 and 1913, *loc. cit.*) that, in the presence of a sufficiently strong acid, a salt of isothiouraea (*b*) was alone presented for attack, and hence formamidine disulphide was produced, thus:



Since the change from (*a*) to (*b*) is likewise promoted by the presence of alkali, oxidation in the presence of the latter should proceed on similar lines. This was found to be the case, but as formamidine disulphide cannot exist in the free state, its chief product of decomposition, namely, cyanamide, was obtained. The yield was 65 per cent. of the theoretical, whilst a certain amount of cyanic acid (as  $\text{NaOCN}$ ) was also formed. The mechanism of this change has yet to be fully studied, but one of the chief points to be noted is that no urea was produced under either of the above conditions.

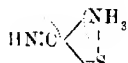
Maly (*Monatsh.*, 1890, **11**, 277) has shown that urea is formed when thiourea is oxidised by potassium permanganate in a neutral solution, and whilst nearly all of the sulphur is oxidised to sulphuric acid, it was noted that the proportion of oxygen fell short of that required by the equation



which was given to represent the change.

A recent statement by Schmidt (*Arch. Pharm.*, 1918, 256, 308), in referring to Maly's experiment, that thiourea is quantitatively changed into urea by potassium permanganate, cannot be upheld.\* Maly distinctly stated that "the yield of urea was deceptive," and, as a matter of fact, only 5 grams of urea (theory = 12 grams) were obtained from 15.2 grams of thiourea, and no explanation was given to account for the deficiency. A repetition of Maly's experiment gave a yield of urea equal to 44.4 per cent. of the theoretical, and whilst 98.7 per cent. of the sulphur was oxidised to sulphuric acid, the amount of potassium permanganate required to decompose the whole of the thiourea was approximately nine-tenths of the theoretical for four atoms of oxygen. Whilst ammonia and a small amount of carbon dioxide were formed as by-products, a crystalline substance having the composition  $C_3H_7N_5$  was isolated. This gave a silver derivative,  $C_3H_5N_5Ag_2$ , and the constitutional formula  $HN:C(NH_2) \cdot C(NH) \cdot C(NH_2) \cdot NH$  is provisionally suggested to explain its formation.

Since urea could not be formed by the oxidation of isothiurea (form *b*), and as there was no evidence of the generation of cyanic acid during the reaction, the production of urea must, in all probability, have resulted from a direct replacement of sulphur by oxygen in the cyclic molecule (form *a*). It seems reasonable to expect that during the progress of such a change, since ammonia was one of the products, some thiourea would be decomposed, thus:



and from the union of  $HN:C$  with two formamidine residues,  $HN:C \cdot NH_2$ , derived from the oxidation of isothiurea (*b*), the compound  $C_3H_7N_5$  would result.

The oxidation of thiourea in neutral solution is therefore in perfect agreement with the views put forward.

#### EXPERIMENTAL.

##### *Interaction of Thiourea and Diazomethane and Diazoethane Respectively.*

*Expt. I.*—1.52 Grams of thiourea and 2.1 grams of nitroso-methylurea were dissolved in 30 c.c. of alcohol which had been

\* A tendency to magnify unduly one change, to the exclusion of all others, has been very prevalent throughout the chemistry of urea, and, in the author's opinion, has been responsible for many of the erroneous conclusions which have been made.



previously dried \* by means of diazomethane. A solution of sodium ethoxide, prepared from 0.46 gram of sodium in 20 c.c. of alcohol, was added. There was at first a feeble evolution of nitrogen, which gradually became quite vigorous as heat was developed, and after about twenty minutes the golden-yellow colour of the solution had completely disappeared.

The solution, freed from the sodium cyanate which had been precipitated (see this vol., p. 1099), was added to 30 c.c. of a cold saturated aqueous solution of picric acid, the alcohol was removed by evaporation, and the sparingly soluble picrate which had separated on cooling was collected and purified by recrystallisation from hot water. It melted at  $221^{\circ}$ , which was also the melting point of the picrate prepared from the product of the action of methyl iodide on thiourea.

*Expt. II.*—This was similar to the above, but 4.2 grams of nitroso-methylurea and 0.92 gram of sodium dissolved in alcohol were used (that is, 2 mols. of diazomethane generated). After the evolution of nitrogen had ceased, the residual liquid had a rich golden-yellow colour, and after twenty-four hours it was dealt with as described under Expt. I, no other picrate than that which melted at  $221^{\circ}$  being isolated from the product. Excess of diazomethane was therefore without action on methylisothiurea.

*Expt. III.*—1.52 Grams of thiourea and 2.35 grams of nitroso-ethylurea were treated as in Expt. I. Similar phenomena were observed, and a picrate was obtained which melted at  $188^{\circ}$ :

0.1897 gave 33.4 c.c.  $N_2$  at  $14^{\circ}$  and 761.5 mm.  $N=20.8$ .

$C_3H_5N_2S_2C_6H_5O_7N$  requires  $N=21.08$  per cent.

A picrate prepared from the product of the interaction of ethyl bromide and thiourea melted at  $188^{\circ}$ .

Experiments with urea, carried out in a similar manner, gave negative results.

#### *Oxidation of Thiourea by Potassium Permanganate.*

*A. In Neutral Solution. Expt. IV.*—To 0.076 gram of thiourea dissolved in 25 c.c. of water, 0.421 gram of potassium permanganate dissolved in 60 c.c. of water was added. After the reaction had been completed in the cold, the product was heated to  $100^{\circ}$ . The filtrate and washings gave  $BaSO_4=0.23$  gram. Theory requires  $BaSO_4=0.233$  gram. Hence 98.7 per cent. of the sulphur was oxidised to  $SO_3$ .

\* A small quantity of a concentrated ethereal solution of diazomethane was added to pure alcohol until the solution retained a pale yellow colour after remaining for twenty-four hours.

*Expt. V.*—22·8 Grams of thiourea were dissolved in 400 c.c. of water, and a hot saturated solution of potassium permanganate was added (about 116 grams were required) until a slight excess of the reagent remained after the product had been heated to 100° for five minutes. The filtrate and washings from the precipitated manganese dioxide were evaporated to dryness at 100°, and the residue was extracted with hot alcohol. After concentration of the latter solution, 1·2 grams of crystals, which had separated in rosette-like conglomerates of slender, glistening prisms, were collected. They were purified from the accompanying urea by recrystallisation from hot alcohol:

0·1868 gave 0·22 CO<sub>2</sub> and 0·1088 H<sub>2</sub>O. C=32·11; H=6·47.

0·1216 „ 64·7 c.c. N<sub>2</sub> at 17° and 765·25 mm. N=62·28.

C<sub>3</sub>H<sub>7</sub>N<sub>3</sub> requires C=31·85; H=6·19; N=61·96 per cent.

The compound decomposed without melting at above 200°, ammonia being evolved. On addition of ammoniacal silver nitrate to the aqueous solution, a bulky, white precipitate was formed.

0·2 Gram dissolved in dilute nitric acid required 12·2 c.c. of N/10-KSCN. Ag=65·88.

C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>Ag<sub>2</sub> requires Ag=66·05 per cent.

Eight grams of nearly pure urea were obtained from the mother liquor of the above compound, equal to 44·4 per cent. of the theoretical.

B. *In Alkaline Solution.* *Expt. VI.*—To 0·152 gram of thiourea dissolved in 25 c.c. of water, 3 c.c. of *N*-sodium hydroxide and 0·842 gram of potassium permanganate dissolved in 100 c.c. of water were added. The oxidation was completed in a few minutes, after which the product was filtered and the precipitated manganese dioxide washed free from all soluble matter. The cyanamide present in the filtrate required 26 c.c. of *N*/10-ammoniacal silver nitrate for precipitation. Cyanamide found=0·0546. Theory requires 0·084. Hence 65 per cent. of the theoretical amount of cyanamide was present. Sodium cyanate, the amount of which was not determined, was also present, but whether this was derived from the direct oxidation of thiourea or from cyanamide first formed has not yet been ascertained. No urea was detected in the solution.

#### *Interaction of Thiourea and Nitrous Acid at Concentration N/30.*

*Expt. VII.*—0·076 Gram of thiourea and 0·072 gram of sodium nitrite were dissolved in 29 c.c. of water in the nitrometer, and 1 c.c. of *N*-acetic acid was added. Evolution of nitrogen at a moderate rate commenced after a few seconds.

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Vol. of  $N_2$  (after forty minutes) = 23.6 c.c. at  $17^\circ$  and 767 mm. = 21.99 c.c. at *N.T.P.* Theory requires  $N_2$  = 22.4 c.c.

Under similar conditions, urea gave no nitrogen even after remaining for three days (compare T., *loc. cit.*).

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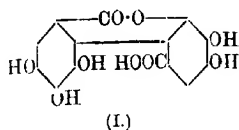
## CVI.—The Tannin of the Knopper Gall.

By MAXIMILIAN NIERENSTEIN.

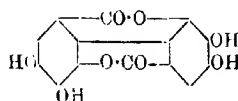
THE "Knopper Galls" (compare E. T. Connold, "Plant Galls of Great Britain," 1909, 254) or "Knopperrn," as they are known in the tanning industry (compare H. R. Procter, "The Principles of Leather Manufacture," 1903, 262), are the galls produced by *Cynips calicis*, Burgsdorff, on the immature acorns of various species of oaks, principally *Quercus cerris* of the Slavonic plains, where these galls are known locally by their Slavonic and Hungarian names, "Ši-arca" and "gubacs" respectively.\* Their occurrence in Great Britain on *Quercus pedunculata* and also *Quercus sessiliflora* has been recorded by E. T. Connold ("British Oak Galls," 1908, 143), who refers to them also as "Gall-nuts." Löwe (*Zeitsch. anal. Chem.*, 1875, 13, 46), who has carried out the only published investigation on knopperrn tannin, described it as being identical with gallotannin. This, however, is not the case, as will be seen from the present communication. It is found that knopperrn tannin yields on hydrolysis, in addition to dextrose, not gallic acid, as is the case with gallotannin, but mainly ellagic acid (II) in common with other "bloom" (ellagic acid) producing

\* I am indebted for some of this information to Dr. Jan Jedlička, whom I have also to thank for the knopperrn used in this investigation. Dr. Jedlička drew my attention to the ease with which the knopperrn extracts deposited ellagic acid which he thought was due to the presence of a ferment in these galls, since he had succeeded in preventing the formation of ellagic acid by prolonged boiling of the extracts. I have attempted to isolate this ferment, but without success. In this connexion I may mention that I also found that emulsin has no effect on knopperrn tannin, which is of interest since this ferment readily hydrolyses the tannin of *Terminalia chebula* into dextrose, luteoic acid, and ellagic acid (*Ber.*, 1910, 43, 1268). On the other hand, I found that *Penicillium* produces ellagic acid from knopperrn tannin which corresponds with the formation of gallic acid from gallotannin by *Penicillium* (compare Knudsen, *J. Biol. Chem.*, 1912, 14, 159; *Anai. J. Coll. Sci. Tokyo*, 1918, 39, 23).

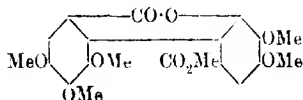
tannins (compare A. G. Perkin and Nierenstein, T., 1905, 87, 1412). It is also observed that methylated knoppern tannin yields on hydrolysis a mixture of partly methylated luteoic acids (I), which give on further methylation with diazomethane methyl pentamethoxyluteoate (III). The latter substance was found to be



(I.)



(II.)



(III.)

identical with the lactone of methyl 2-hydroxy-3:4:4':5':6'-penta-methoxydiphenyl-6:2'-dicarboxylate (III), previously described by Herzog and Polack (*Monatsh.*, 1908, 29, 263). From these observations it is provisionally concluded that the knoppern tannin molecule is composed of luteoic acid (I) and dextrose, the luteoic acid being predominant. Luteoic acid, which is an oxidation product of gallotannin (*Ber.*, 1908, 41, 3015), has also been found to be the predominant component of the tannin of *Terminalia chebula* (*Ber.*, 1910, 43, 1267). Reference ought also to be made to the presence of galloyl-L-leucine in the fat extracted from the knopper gall (*Zeitsch. physiol. Chem.*, 1914, 92, 53), and the production of ellagic acid from galloylglycine by *Penicillium* (*Biochem. J.*, 1915, 9, 240), which observations, in conjunction with the suggested configuration of knoppern tannin, may be regarded as further evidence in support of the assumption made (*Biochem. J.*, 1915, 9, 241) that some nitrogenous galloyl derivatives serve as foodstuffs for the growing, gall-producing parasites and at the same time lead to the formation of "pathological" tannins, such as gallo-tannin, knoppern tannin, and the other tannins found in galls (compare Nierenstein, *Ber.*, 1910, 43, 628; Drabble and Nierenstein, *Biochem. J.*, 1907, 2, 96; Nierenstein and Webster, *Ber.*, 1908, 41, 80).

#### EXPERIMENTAL.

##### *Preparation of Knoppern Tannin.*

The powdered and finely sieved knoppern were at first extracted with boiling chloroform or *s*-tetrachloroethane, so as to remove the

so-called gall-fats.\* The carefully dried powder was subsequently extracted with boiling acetone. In both cases the extraction was carried out in the extraction apparatus described elsewhere (Abderhalden, "Handbuch der biochemischen Arbeitsmethoden," 1912, 6, 149). The acetone extract was made up to 1.5 litres and the tannin precipitated with 300 c.c. of light petroleum which had been dried over calcium chloride. The crude tannin obtained in this way was purified by dissolving 50 grams of it in 1 litre of acetone and precipitating with four successive quantities of light petroleum of 100 c.c. each. It is necessary to dry both the acetone and the light petroleum over calcium chloride for some time, as otherwise the products obtained are viscid (compare also Manning and Nierenstein, this vol., p. 666). The fractions obtained weighed 26, 12, 6, and 2.5 grams respectively and were pale-coloured, amorphous products which neither melted nor decomposed when heated above 300°. They were soluble in alcohol, acetone, ethyl acetate, acetic acid, or water, but insoluble in benzene, light petroleum, or chloroform. The different solutions gave greenish-blue colorations with ferric chloride, which were particularly well-marked when the alcoholic solution was employed. This is of special interest in view of the generally accepted classification of the tannins into catechol and pyrogallol groups, which classification is based on the green and blue colorations given by these two groups respectively with ferric chloride. In this connexion it ought to be mentioned that the tannins of *Terminalia chebula* (Nierenstein, *loc. cit.*) and *Polygonum bistorta* (Stenhouse, *Phil. Mag.*, 1843, [iii], 23, 335; Eissfeld, *Annalen*, 1854, 92, 109; 1859, 111, 217; Bjalobreshesky, *Pharm. J.*, 1900, 22, 3; Jlijn, *Diss.*, Petrograd, 1905, p. 38) show similar mixed colorations with ferric chloride. The aqueous solution of knoppern tannin precipitates alkaloids and gelatin, and is quantitatively adsorbed by caseinogen (compare Manning and Nierenstein, this vol., p. 667). Knoppern tannin is hygroscopic, and the determination of its elementary composition by combustion requires the same precautions as used by Geake and Nierenstein (*Ber.*, 1914, 47, 897) in the analysis of gallotannin.

Found:

Fraction I.—C=54.3; H=2.1. M.W. (in acetone)=1628, 1654, 1708. M.W. (in alcohol)=1744, 1682, 1664.

\* Preliminary investigations of the gall-fats of the knoppern seem to indicate that they are identical with the fats derived from Aleppo galls (compare Kunz-Krause and his collaborators, *Apoth. Zeit.*, 1897, 37, 734; *Arch. Pharm.*, 1904, 237, 256; 1907, 245, 28). These observations refer mainly to cyclogallipharic acid of the knoppern gall-fat, which had been obtained by Kunz-Krause's method. It crystallised, like his cyclogallipharic acid, from light petroleum in large scales melting at 88—89°.

Fraction II.— $C=54.1$ ;  $H=2.2$ .

Fraction III.— $C=55.4$ ;  $H=2.4$ . M.W. (in acetone)=1758, 1744, 1694. M.W. (in alcohol)=1742, 1716, 1758, 1708.

Fraction IV.— $C=55.6$ ;  $H=2.5$ . M.W. (in acetone)=1702, 1744, 1726. M.W. (in alcohol)=1758, 1744, 1726.

For the polariscopical investigations of knoppern tannin only 0.5 per cent. solutions were used in view of the experiences of Navassarat (*Kolloid Zeitsch.*, 1913, **12**, 97) in the case of gallo-tannin:

Fraction I.— $[\alpha]_D^{25} + 31.8^\circ$  (in alcohol);  $+ 8.4^\circ$  (in acetone).

Fraction IV.— $[\alpha]_D^{25} + 36.2^\circ$  (in alcohol);  $+ 11.8^\circ$  (in acetone);  $+ 28.6^\circ$  (in water).

#### *Hydrolysis of Knoppern Tannin.*

About 0.5 gram of knoppern tannin (Fractions III and IV only were used) was dissolved in 200 c.c. of water and heated with 20 c.c. of a 5 per cent. solution of sulphuric acid for eight to twelve hours on a water-bath, a reflux condenser being used. The ellagic acid formed was collected in a Gooch crucible and washed at first with cold water, so as to remove all traces of sulphuric acid, and afterwards with alcohol and ether. The precipitate was dried at  $130^\circ$  and weighed as ellagic acid. (Found,  $C=56.4$ ,  $55.8$ ;  $H=2.1$ ,  $2.2$ . Calc.,  $C=55.6$ ;  $H=2.0$  per cent.) The filtrate was tested for dextrose by Fischer and Freudenberg's method (*Ber.*, 1912, **45**, 915) and the dextrose was estimated volumetrically by Bertrand's method (*Bull. Soc. chim.*, 1906, [iii], **35**, 1286) as used by Nierenstein and Geake (*loc. cit.*) for the estimation of dextrose in gallo-tannin. In addition to this, the dextrose was also estimated polariscopically, in one case after the hydrolysis of 12.8 grams of knoppern tannin. The dextrosazone was also prepared and found to have the correct melting point. (Found,  $N=15.9$ . Calc.,  $N=15.6$  per cent.)

Found: Ellagic acid=84.6, 72.4, 81.2, 78.4. Dextrose=7.2, 6.4, 5.8, 6.7 (by Bertrand's method), 7.8 (polariscopically) per cent.

#### *Methylated Knoppern Tannin.*

The methylation (Fractions III and IV only were used) was carried out with diazomethane in ethereal suspension, and the same precautions were taken as in the case of hemlock tannin (compare Manning and Nierenstein, *loc. cit.*). The methylated knoppern tannin dissolved completely in the ether and was purified several

times by dissolving it in alcohol and precipitating with water. The methylated knoppern tannin obtained in this way was a colourless, amorphous product without any definite melting point. It was soluble in alcohol, acetone, chloroform, or *s*-tetrachloroethane, but insoluble in water or light petroleum.

Found: C=58.8, 57.9, 58.2; H=4.1, 4.4, 4.3; OMe=36.9, 37.4, 37.2, 37.8. M.W. (in alcohol)=1822, 1848, 1912. M.W. (in acetone)=1894, 1826, 1858.

The methoxyl estimations were carried out in a Zeisel-Perkin apparatus, acetic anhydride being added. If the latter was replaced by phenol (compare Weishut, *Monatsh.*, 1913, **33**, 1165) the same result (OMe=36.5) was obtained.

For the polariscopical investigations only 0.5 per cent. solutions were used, and the results obtained were as follows:

Found:  $[\alpha]_D^{25} + 4.2^\circ$  (in alcohol);  $+ 6.8^\circ$  (in acetone);  $+ 16.2^\circ$  (in chloroform);  $+ 28.2^\circ$  (in *s*-tetrachloroethane).

#### *Alkali Hydrolysis of Methylated Knoppern Tannin.*

Methylated knoppern tannin (about 5–10 grams) was hydrolysed by boiling with a 10 per cent. solution of alcoholic potassium hydroxide for eight hours, a reflux condenser being used. The alcohol was then evaporated and the residue extracted with boiling water, the extract being filtered from any unchanged or tarry material. On acidifying the cold solution with dilute sulphuric acid, there was obtained a bulky, colourless precipitate (Precipitate A), which was collected, washed, and dried in a desiccator. The filtrate was extracted several times with ether, which left on evaporation a tarry residue. Several attempts were made to isolate a definite disintegration product from this residue, but without success. The average yield of this residue corresponded with about 22 per cent. of the material hydrolysed. It did not reduce Fehling's solution.

*Precipitate A.*—This product proved to be a mixture, and it was found possible to separate it into two parts, respectively soluble and insoluble in benzene. The carefully dried substance was extracted in a Soxhlet apparatus with benzene, until a few drops of the overflow left no residue on evaporation. Five grams of the precipitate left about 2 grams in the thimble (Fraction I). The benzene solution gave on evaporation a second product (Fraction II). Both fractions were investigated separately.

*Fraction I.*—This product had no definite melting point ( $67$ – $84^\circ$ ), and it was found impossible to crystallise it. The investigation of this amorphous material disclosed the following interest-

ing points, which might, perhaps, in time, prove of importance in the chemistry of knoppern tannin. It was found that the alcoholic solution gave a pronounced green coloration with ferric chloride, thus indicating (1) that it contained two hydroxyl groups in the ortho-position, and (2) that these two hydroxyl groups escaped methylation during the action of diazomethane on knoppern tannin. Attempts were also made to oxidise the alcoholic solution with silver oxide (Willstätter and Pfannenstiel, *Ber.*, 1904, **37**, 4744) or *p*-benzoquinone (A. G. Perkin, *T.*, 1913, **103**, 661; Nierenstein, *T.*, 1915, **107**, 860) in the hope of obtaining the corresponding *o*-quinone. These experiments, however, only gave negative results.

Found: C=56.8, 57.1; H=4.4, 4.2; OMe=27.8, 26.4, 27.3.

These analytical data indicated that Fraction I was still a mixture consisting of tetramethoxyluteoic acid (Calc., C=57.4; H=4.2; OMe=32.9 per cent.) and trimethoxyluteoic acid (Calc., C=56.3; H=3.8; OMe=25.6 per cent.), the latter being predominant.

That Fraction I was a mixture was also proved on acetylation with acetyl chloride and pyridine. The acetyl derivative was also amorphous, and decomposed on heating at about 129–135°. Only acetyl estimations by A. G. Perkin's method (*T.*, 1905, **87**, 107) were made, which gave Ac=14.5, 13.8, 14.2 per cent., whereas the mono- and the di-acetyl derivatives require Ac=10.2 and 19.3 per cent. respectively.

On further methylation with diazomethane in ethereal solution Fraction I was entirely converted into methylpentamethoxyluteoate (III), which crystallised from alcohol in small needles melting at 110°; this is in the vicinity of the melting point, 109–111°, given by Herzig and Polack (*loc. cit.*) for this substance. For comparison, the acid was also prepared by the method described by these authors from ellagic acid, when it was also found to melt at 110°. There was no depression of the melting point when the two preparations were mixed. (Found, C=59.1; H=5.1; OMe=46.3.  $C_{20}H_{20}O_9$  requires C=59.4; H=4.9; OMe=46.1 per cent.)

*Fraction II.*—This fraction did not give clearly the colour reaction with ferric chloride mentioned above, but the analytical data obtained for it agreed on the whole better for tetramethoxyluteoic acid than for trimethoxyluteoic acid, although in view of the amorphous character of the product and its indefinite melting point, which was found to be 98–112°, it seems obvious that the material was not pure. (Found, C=57.8, 57.6; H=4.5, 4.7; OMe=31.7, 31.4, 31.6.  $C_{18}H_{16}O_9$  requires C=57.4; H=4.2; OMe=32.9 per cent.)



It was found possible to acetylate Fraction II with acetyl chloride and pyridine, but a satisfactory product was not obtained. (Found, Ac=11.8, 12.2, 12.0. Calc., Ac=10.2 per cent.)

On further methylation with diazomethane, Fraction II was entirely converted into methyl pentamethoxyluteoate (III); small needles melting at 110° were obtained, and this melting point was not changed by admixture with Herzig and Polack's product. (Found, C=59.2; H=4.9; OMe=46.1. Calc., C=59.4; H=4.9; OMe=46.1 per cent.)

This investigation has, with many interruptions, been in progress since 1907, during which time the author has had the collaboration of Dr. D. Spence and Messrs. R. J. Thompson, J. F. Fielding, C. W. Spiers, and F. S. Wallis, for which he wishes to thank them. The author is also indebted to the Research Fund Committee of the Chemical Society and the Colston Society of the University of Bristol for grants in aid of this investigation.

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## CVII.—*The Oxidation of Phenol Derivatives.*

By CYRIL NORMAN HINSHELWOOD.

THE observation that phenol in aqueous solution is completely and instantly oxidised by potassium permanganate whilst picric acid is very much more stable led to the examination of a number of other phenol derivatives. The mononitrophenols and the hydroxybenzoic acids are, like phenol itself, attacked by  $N/10$ -potassium permanganate with great rapidity. Bradshaw (*Amer. Chem. J.*, 1906, 35, 326) carried out experiments from which he concluded that the order of attack at 0° was ortho, meta, para in acid solution and meta, ortho, para in alkaline solution. This is in accord with some older results of Dreyfus (*Compt. rend.*, 1887, 105, 523).

Care must be exercised in drawing conclusions as to stability from the rate at which potassium permanganate is destroyed. The oxidation occurs in a series of stages of which only the first involves the breaking of the ring. Consequently, the initial rate of oxidation is the true measure of stability and the later stages are of minor importance. It is, of course, necessary to avoid complications due to the oxidation of side chains.

The method adopted for measuring the rate of oxidation was as follows. Aqueous solutions of the substances to be tested were prepared of such strength that for complete oxidation to carbon dioxide and water (and nitric acid in the case of nitro-compounds) an equal volume of  $N/10$ -potassium permanganate would be required. In making the calculation it was assumed that five atoms of oxygen would be yielded by the permanganate. Twenty-five c.c. of the solution were mixed with 50 c.c. of  $N/10$ -potassium permanganate and 10 c.c. of  $N/5$ -sulphuric acid in a thermostat adjusted to  $25.0^{\circ}$  and allowed to react for a measured time. The reaction was then stopped by the addition of potassium iodide and the liberated iodine titrated with  $N/10$ -sodium thiosulphate. As a matter of fact the potassium permanganate only yielded three atoms of oxygen, and brown oxide of manganese was always precipitated. As, however, double the amount was used which would be required if five atoms were given up, there was still an excess even when only three atoms were yielded. Moreover, the estimation of the iodine liberated gave results directly in terms of oxygen employed, independently of the actual state to which the manganese was reduced, so that complete oxidation still corresponded with a diminution of the thiosulphate titre of the mixture by 25 c.c. Two further points may be mentioned. Gooch has pointed out that acid solutions of potassium permanganate slowly lose oxygen. It was ascertained by blank determinations that no loss occurred in the longer experiments from this cause. Secondly, although the presence of any considerable amount of nitric acid is very undesirable in working with sodium thiosulphate, the concentration of that produced by the oxidation of the nitro-compounds was not sufficient to vitiate the results in any way. It was only necessary to ensure by efficient shaking that the thiosulphate did not remain in local excess during the titration.

Some results obtained with salicylic acid and with *p*-nitrophenol may be quoted first, as they serve to illustrate the complex course of the reaction and the condition for a good measure of stability.

The salicylic acid was recrystallised from water, and the *p*-nitrophenol was recrystallised twice from water and from hydrochloric acid. The pipettes and burettes were standardised, and the potassium permanganate and sodium thiosulphate solutions compared with each other daily.

The thermostat remained constant to about  $0.01^{\circ}$ .

## (1) Salicylic acid.

0.4929 gram per litre.

25 c.c. Salicylic acid solution

50 c.c.  $N/10$ - $KMnO_4$ 10 c.c.  $N/5$ -Sulphuric acid

| Time in minutes.  | Amount of oxygen used up in terms of c.c. $N/10$ - $Na_2S_2O_3$ |
|---|---|
| 0.5   | 16.6  |
| 1.5   | 18.05   |
| 3.5   | 18.53   |
| 21  | 19.60   |
| 37  | 20.15   |
| 110   | 22.0  |
| 150   | 22.20   |
| 320   | 23.18   |
| $\infty$ (theor.) for complete oxidation to carbon dioxide and water. | 25.0  |

(2) *p*-Nitrophenol.

0.496 gram per litre.

25 c.c. *p*-Nitrophenol solution50 c.c.  $N/10$ - $KMnO_4$ 10 c.c.  $N/5$ -Sulphuric acid.

| Time in minutes.  | Amount of oxygen used up in terms of c.c. $N/10$ - $Na_2S_2O_3$ |
|---|---|
| 0.55  | 13.2  |
| 3.0   | 14.75   |
| 13.5  | 17.2  |
| 24.5  | 17.5  |
| 30  | 17.6  |
| 38  | 18.13   |
| 43  | 18.45   |
| 54.5  | 19.38   |
| 61.5  | 20.03   |
| 75.5  | 20.57   |
| $\infty$ (theor.) for complete oxidation to carbon dioxide, nitric acid, and water. | 25.0  |

It is clear that we have to deal in each case with consecutive reactions, the first stage of which is almost immeasurably rapid. Differences in the later stages will depend on the nature of the intermediate open-chain products, and throw no light on the stability of the original compound. This point does not seem to have received sufficient attention from Dreyfus and Bradshaw.

With the more highly substituted phenols quite trustworthy measurements can be made, and comparisons of stability obtained. Picric acid was taken as a standard of reference.

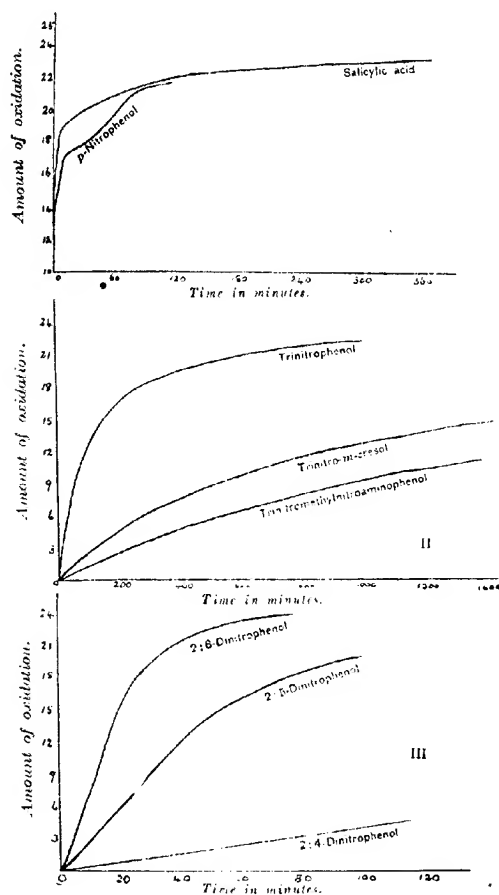
*Picric Acid*.—"Pure" picric acid was recrystallised twice from water. The solution contained 0.818 gram per litre.

(3) Picric acid                      25 c.c.  
 $N/10$ - $KMnO_4$                       50 c.c.  
 $N/5$ -Sulphuric acid                10 c.c.

| Time in minutes.  | Amount of oxygen used up in terms of c.c. $N/10$ - $Na_2S_2O_3$ . | $k$ (see below). |
|-------------------|---|------------------|
| $t$ .             | $x$ .   |                  |
| 15                | 2.95  | 0.000130         |
| 26.25             | 4.68  | 0.000125         |
| 45                | 6.98½   | 0.000122         |
| 83                | 10.50   | 0.000119         |
| 120               | 12.98   | 0.000120         |
| 208               | 16.10   | 0.000110         |
| 255.8             | 17.12   | 0.000105         |
| 930               | 21.80   | —                |
| 2340              | 23.0  | —                |
| $\infty$ (theor.) | 25.0  | —                |

Mean 0.000119

In calculating  $k$  it is assumed that the permanganate yields three atoms of oxygen, so that its concentration is initially proportional



to  $3.5 \times 50 = 30$ . The initial concentration of the picric acid is proportional to 25, and

$$k = \frac{1}{(30 - 25)t} \log_{10} \frac{5(30 - x)}{6(25 - x)}$$

being calculated for a reaction of the second order and its value

being fairly constant over the whole range, there is little evidence here of consecutive reactions. Evidently the first stage, namely that involving the rupture of the ring, proceeds more slowly than the subsequent reactions. This accounts for the simple nature of the effect, and is confirmed by the fact that the later stages in the oxidation of *p*-nitrophenol and salicylic acid are more rapid than the corresponding stage of the picric acid reaction.  $k$  then is a measure of the stability of the picric acid molecule towards oxidation.

The effect of dilution was examined, so that less readily soluble substances might subsequently be compared with picric acid, using more dilute solutions. Incidentally, the results confirm the bimolecular nature of the change.

|                                |         |                                |          |
|--------------------------------|---------|--------------------------------|----------|
| (4) Picric acid solution       | 25 c.c. | (5) Picric acid solution       | 25 c.c.  |
| <i>N</i> /10-KMnO <sub>4</sub> | 50 c.c. | <i>N</i> /10-KMnO <sub>4</sub> | 50 c.c.  |
| <i>N</i> /5-Sulphuric acid     | 10 c.c. | <i>N</i> /5-Sulphuric acid     | 10 c.c.  |
|                                | 85 c.c. |                                | 85 c.c.  |
| + water                        | 85 c.c. | + water                        | 170 c.c. |

| $k = \frac{2}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$ |          |          | $k = \frac{3}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$ |          |          |
|--|----------|----------|--|----------|----------|
| <i>t</i>   | <i>x</i> |          | <i>t</i>   | <i>x</i> |          |
| 60   | 5.05     | 0.000120 | 162  | 7.22     | 0.000105 |
| 156.5  | 9.65     | 0.000111 | 446  | 13.23    | 0.000100 |
| 240  | 12.45    | 0.000111 | 581  | 14.98    | 0.000100 |
| 305  | 13.87    | 0.000107 |  |          |          |
| 435  | 15.97    | 0.000103 |  |          |          |
| Mean   |          | 0.000110 |  |          |          |

|                                |          |
|--------------------------------|----------|
| (6) Picric acid solution       | 25 c.c.  |
| <i>N</i> /10-KMnO <sub>4</sub> | 50 c.c.  |
| <i>N</i> /5-sulphuric acid     | 10 c.c.  |
|                                | 85 c.c.  |
| + water                        | 255 c.c. |

| $k = \frac{4}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$ |          |
|--|----------|
| <i>t</i>   | <i>x</i> |
| 213  | 6.85     |
| 583  | 12.50    |

The bimolecular constant diminishes somewhat with dilution.

2:4:6-*Trinitro-m-cresol*.—This was prepared by the thorough nitration of *m*-cresol (98 per cent.), and recrystallised three times from alcohol. A solution containing 0.7150 gram per litre was employed.

- (8) 25 c.c. Trinitrocresol solution.  
50 c.c.  $N/10\text{-KMnO}_4$ .  
10 c.c.  $N/5\text{-Sulphuric acid}$ .

| Time<br>in minutes. |  | Amount of oxygen<br>used up in terms<br>of c.c. | $k = \frac{1}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$ |
|---------------------|--|---|--|
| $t$                 | $N/10\text{-Na}_2\text{S}_2\text{O}_4$ | $x$   |  |
| 30                  | 0.75                                   | —   | —  |
| 77                  | 1.85                                   | —   | 0.0000149  |
| 86                  | 2.05                                   | —   | 0.0000149  |
| 246                 | 5.05                                   | —   | 0.0000146  |
| 405                 | 7.25                                   | —   | 0.0000141  |
| 592                 | 9.25                                   | —   | 0.0000137  |
| 1006                | 12.53                                  | —   | 0.0000134  |
| 1355                | 14.28                                  | —   | 0.0000120  |
| $\infty$ (theor.)   | 25.0                                   | —   | —  |

Mean 0.0000141

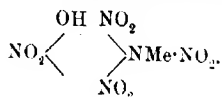
The results are completely parallel to those obtained with picric acid—the same bimolecular law and the same slight decrease in velocity constant with time. This similarity in the dynamics of the two reactions shows, as one would expect, that a preliminary oxidation of the methyl to the carboxyl group does not disturb matters.

The ratio of the mean values of  $k$  is, then, a measure of the relative stability of the two compounds. We have:

$$\frac{k \text{ for trinitrocresol}}{k \text{ for picric acid}} = \frac{0.0000141}{0.000119} = 0.118,$$

that is, trinitrocresol is only 0.118 times as reactive towards potassium permanganate as picric acid, or is 8.5 times as stable as picric acid.

2:4:6-Trinitro-3-methylnitroaminophenol,



It was thought of interest to examine this compound as an example of a very heavily substituted phenol. It was prepared by the nitration of methylaniline in the presence of excess of concentrated sulphuric acid, followed by hydrolysis of the tetranitro-3-methylnitroamino-compound, which is one of the principal primary products. It was purified by several recrystallisations from acetone and from water, and its purity checked by acidimetric titration. A solution containing 0.757 gram per litre was employed.

- (9) 25 c.c. Solution,  
50 c.c.  $N/10\text{-KMnO}_4$ ,  
10 c.c.  $N/5\text{-Sulphuric acid}$

| Time in minutes. | $x$ . | $k = \frac{1}{(30-25)t} \log_{10} \frac{5(30-x)}{6(25-x)}$ |
|------------------|-------|--|
| $t$ .            |       |  |
| 180              | 2.55  | 0.00000904   |
| 351              | 4.43  | 0.00000872   |
| 372              | 4.60  | 0.00000881   |
| 1485             | 11.90 | 0.00000825   |
|                  |       | Mean 0.00000865  |

$$\frac{k}{k_{\text{picric}}} = \frac{0.00000865}{0.000119} = 0.0725.$$

The reactivity towards potassium permanganate is thus 0.0725 times that of picric acid, or the compound is 13.8 times as stable. Here, again, the similarity between the dynamics of this reaction and the picric acid reaction may be taken to show that the side chain does not suffer attack before the ring is broken. (See Fig. II.)

#### Dinitrophenols.

In the case of three dinitrophenols curves of a somewhat different type were obtained. I am greatly indebted to Mr. Aldous, who kindly supplied me with pure specimens of the compounds used.

The solutions (0.3285 gram per litre) were of half the strength used in the previous experiments, and the potassium permanganate and acid correspondingly of half strength.

#### (10) 2:6-Dinitrophenol.

50 c.c. Dinitrophenol solution.  
100 c.c.  $N/20\text{-KMnO}_4$ ,  
20 c.c.  $N/10\text{-Sulphuric acid}$ .

| Time in minutes.  | Amount of oxygen used up in terms of c.c. $N/10\text{-Na}_2\text{S}_2\text{O}_3$ . | $x/t$ . |
|---|--|---------|
| $t$ .   | $x$ .  |         |
| 5   | 3.40   | 0.680   |
| 7.7   | 5.33   | 0.693   |
| 10  | 7.05   | 0.705   |
| 15.5  | 11.00  | 0.709   |
| 18.3  | 13.17  | 0.720   |
| 20  | 14.48  | 0.724   |
| 27.3  | 17.70  | —       |
| 44.6  | 21.5   | —       |
| 330   | 24.25  | —       |
| $\infty$ (theor.) for complete oxidation to carbon dioxide, nitric acid, and water. | 25.0   | —       |

#### (11) 2:4-Dinitrophenol.

50 c.c. Dinitrophenol solution.  
100 c.c.  $N/20\text{-KMnO}_4$ ,  
20 c.c.  $N/10\text{-Sulphuric acid}$ .

| Time in minutes. | Amount of oxygen used up in terms of c.c. $N/10\text{-Na}_2\text{S}_2\text{O}_3$ . | $x/t$ . |
|------------------|--|---------|
| $t$ .            | $x$ .  |         |
| 11.3             | 0.26   | —       |
| 150              | 5.60   | 0.0373  |
| 206              | 8.0  | 0.0388  |
| 307              | 11.60  | 0.0378  |
| 422              | 15.86  | —       |
| $\infty$         | 25.0   | —       |

(12) 2:5-Dinitrophenol.  
50 c.c. Dinitrophenol solution.  
100 c.c.  $N/20\text{-KMnO}_4$ .  
20 c.c.  $N/10\text{-Sulphuric acid}$ .

| Oxygen used up in terms of c.c. |  |         |
|---------------------------------|--|---------|
| Time in minutes.                | $N/20\text{-Na}_2\text{S}_2\text{O}_5$ . | $x/t$ . |
| 16                              | 4.67                                     | 0.292   |
| 23.5                            | 6.67                                     | 0.284   |
| 31                              | 9.12                                     | 0.294   |
| 41                              | 12.45                                    | 0.304   |
| 55                              | 14.57                                    | 0.265   |
| 68                              | 16.87                                    | —       |
| 87                              | 19.00                                    | —       |
| 155                             | 21.79                                    | —       |
| $\infty$                        | 25.0                                     | —       |

The form of the curves is quite different from that obtained with picric acid. The reactions are autocatalytic, a point which will be referred to again later. The approximate constancy of  $x/t$  over a considerable range has little theoretical bearing, but enables the initial velocity to be calculated in each case.

Initial rate of oxidation in c.c. per minute for 2:6-dinitrophenol = 0.705.

Initial rate of oxidation in c.c. per minute for 2:4-dinitrophenol = 0.0379.

Initial rate of oxidation in c.c. per minute for 2:5-dinitrophenol = 0.294.

The corresponding initial rate for picric acid in the same units may be found by evaluating  $dx/dt$  for  $t=0$  from the expression in Expt. 4 (half strength picric acid):

$$\frac{2}{(30-25)t} \log_{10} \frac{(30-x)}{(25-x)} = k_2 = 0.000110.$$

hence

$$\left(\frac{dx}{dt}\right)_0 = 0.0950.$$

Approximate experiments further give a lower limit for the initial rates in the case of phenol and some mono-derivatives. The results are combined in the table below:

| Compound.                          | Relative rate of oxidation. | Relative stability of ring. |
|------------------------------------|-----------------------------|-----------------------------|
| Phenol                             | ~ 500                       | ~ 0.002                     |
| Salicylic acid                     |                             |                             |
| <i>o</i> -Nitrophenol              | ~ 250                       | ~ 0.004                     |
| <i>m</i> -Nitrophenol              |                             |                             |
| <i>p</i> -Nitrophenol              |                             |                             |
| 2:6-Dinitrophenol                  | 7.4                         | 0.135                       |
| 2:4-Dinitrophenol                  | 0.40                        | 2.50                        |
| 2:5-Dinitrophenol                  | 3.09                        | 0.324                       |
| Picric acid                        | 1.00                        | 1.00                        |
| 2:4:6-Trinitro- <i>m</i> -cresol   | 0.118                       | 8.5                         |
| Trinitromethylnitroaminophenol ... | 0.073                       | 13.8                        |



Taking into consideration the nature of the curves, it is thought that these figures give a true measure of the relative stability of the ring in the various compounds. If the initial velocity were in any case that due to the formation of another aromatic derivative indications of consecutive reactions would be found. In the only cases where these were found, namely, phenol and its mono-derivatives, the first rapid change was far too profound to be other than a complete decomposition of the aromatic nucleus.

In general, whilst phenol and its mononitro- and carboxy-derivatives are extraordinarily unstable towards potassium permanganate, the more heavily substituted compounds have acquired considerable stability. There is no definite connexion between rate of oxidation and degree of ionisation. The instability of phenol renders a true aromatic constitution improbable. It may be provisionally suggested that the reactivity is due to the production of

the tautomeric keto-form,  $\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{H}_2$ , or, in accordance with

the principle of Baly and Stewart, to the actual oscillation between this and the normal form. Heavy substitution might be expected to inhibit tautomerisation and to depress the reactivity. On this view the autocatalytic reaction in the case of the dinitrophenols could be simply explained. The yellow solutions of these compounds are decolorised by moderate amounts of sulphuric acid. This may well be due to the repression of a quinonoid keto-form. As oxidation proceeds sulphuric acid enters into the reaction, and the keto-form can reappear. Hence the acceleration.

In conclusion, I wish to thank Mr. D. H. Nagel, M.A., for the interest he has taken in these experiments.

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### CVIII.—Chloropicrin. Part I.

By JOHN ADDYMAN GARDNER and FRANCIS WILLIAM FOX.

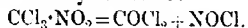
WHEN commercial chloropicrin, purified by distillation in a current of steam and dried over calcium chloride until it no longer restores the blue colour to anhydrous copper sulphate, is distilled under atmospheric pressure, it boils at about  $112^\circ$ , and a small amount of a yellowish-red gas, recalling in appearance diluted nitrous fumes,

is always evolved which is seen in the atmosphere of the condenser and receiver. After several redistillations the distillate and the chloropicrin remaining in the flask were found on analysis to contain the same percentage of chlorine.

No mention of this phenomenon could be found in the literature. Stenhouse (*Annalen*, 1848, **66**, 241) states that the substance distills unchanged at 120°, and can be heated to 150° without undergoing decomposition, but if the vapour is passed through a heated glass flask, at a temperature below red heat, it decomposes completely, chlorine and nitric oxide being evolved and a quantity of perchloroethane being deposited in the cooler part of the flask. Hofmann (*Annalen*, 1866, **139**, 111) gives the boiling point 112°, and Thorpe (T., 1880, **37**, 198) 111·91°, but neither observer mentions any decomposition. Cossa (*Gazzetta*, 1872, **2**, 181) gives the boiling point 112·8°, and states that the substance explodes when rapidly heated or when the vapour is led into a red-hot tube. Levy and Jedlicka (*Annalen*, 1888, **249**, 86) state that bromopicrin explodes on distillation under the ordinary pressure, giving red fumes, but that it can be distilled unchanged under diminished pressure. In the article on chloropicrin in Wurtz's "Dictionnaire de Chimie," the writer states that "elle bout à 120°; à 112° (Hofmann): elle supporte une température de 150° sans se décomposer; surchauffée sa vapeur fait une violente explosion."

It seemed of interest, therefore, to submit the phenomenon to closer investigation.

When chloropicrin was caused to explode by heat or otherwise, a strong odour of carbonyl chloride was always noticed. This fact, together with the constancy of composition after boiling, suggested that chloropicrin at its boiling point slowly decomposes into carbonyl chloride and nitrosyl chloride:



This was found to be the case, and 200 c.c. of that liquid, kept very gently boiling, decomposed at the rate of about 2 c.c. per day.

This observation is of interest for a variety of reasons. It throws light on the rather divergent statements that have been made on the physiological activity of chloropicrin. In making experiments on this subject, the mixture of chloropicrin vapour and air to be tested on animals should be made either by atomising the liquid into the air or by evaporating at a low temperature; if the mixture were made by boiling the chloropicrin, or by bursting a bomb by any means, the atmosphere produced would contain chloropicrin vapour more or less contaminated with carbonyl chloride and nitrosyl chloride, and if the air were damp perhaps also nitrous fumes, so that a mixed result would be obtained.

It also throws light on many of the chemical reactions of chloropicrin, which is a very reactive substance. It has already been pointed out by Frankland, Challenger, and Nicholls (this vol., p. 159) that under some conditions chloropicrin is reduced quantitatively to methylamine, but under others to ammonia, etc. Obviously in the first case it is reduced as such, and in the latter the decomposition products are reduced.

There are many other reactions in which chloropicrin behaves as an oxidising agent. In some it appears to react as a nitro-compound; for instance, it can be used to replace nitrobenzene in Skraup's method of preparing quinoline, in others the results can be explained as due to the decomposition products. We hope shortly to have the honour of bringing before the Society a detailed account of some of these reactions.

This decomposition may also account for the varied yields obtained by different observers in the production of chloropicrin by the action of bleaching powder on picric acid. By proper attention to the proportions of the reagents and the conditions of reaction yields of 180—190 per cent. of the picric acid used can easily be obtained on a technical scale,\* but if the optimum conditions are not strictly adhered to the yield may easily sink to 130 per cent., or even to 114 as given originally by Hofmann, or less.

#### EXPERIMENTAL.

Chloropicrin, in quantities of about 200 c.c., was boiled, on a sand-bath, in a 300 c.c. flask with a long neck and provided with a long reflux condenser. The end of the condenser was connected to a series of wash-bottles containing the reagents for absorbing the

\* The proportions found to be best for obtaining yields of about 180 per cent. were 10 parts of picric acid to 100 parts of bleaching powder. The exact proportion, however, depends on the quality of the latter. The material used generally contained about 33 per cent. of available chlorine. The method adopted was to carry out a trial distillation with the above proportions. If it was found in the trial distillation that the effluent was at all yellow the amount of picric acid was lessened. If it was found that there was any tendency to frothing, a little extra was added. This was found to be a much more satisfactory method of work than attempting to estimate each batch of bleaching powder. The best conditions for the reaction are for the bleaching liquor to be about 30°, when on the addition of solid picric acid the temperature very rapidly rises to distilling point and steam is only used in the final stage of the reaction to carry over the last traces of chloropicrin. Contrary to statements frequently made, no artificial means of evading frothing is of any practical use. Once frothing commences badly, the yield steadily diminishes. On the large scale, the only way of destroying froth is to add a further small quantity of solid picric acid, a somewhat unpleasant, not to say dangerous operation.

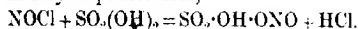
products of decomposition. The various parts of the apparatus were joined either by ground-glass joints or by sealing in the blow-pipe.

In the earlier experiments the wash-bottles were charged with 40—50 per cent. potassium hydroxide solution to absorb the whole of the products of decomposition. At the end of an experimental period the contents of the bottles were diluted to definite volume and estimations were made of the carbonate, nitrite, and chloride present. The method did not prove quite satisfactory, as the connecting tubes were apt to become clogged with crystalline matter deposited from the concentrated alkaline solution. It also proved difficult to obtain complete absorption of the carbonyl chloride. The latter difficulty was overcome by charging the last bottle with  $N/2$ -alcoholic potassium hydroxide. Owing to the large bulks of concentrated alkali hydroxide required, and the long duration of the experiments, it proved troublesome to make very exact corrections for the chlorides and carbonates contained in the original potassium hydroxide.

In two experiments the ratio  $CO_2:NO_2:Cl$  was found to be 1:1.003:2.14 and 1:0.993:2.42 respectively. The theoretical ratio is 1:1.046:2.42.

In subsequent experiments the constituents of the mixture were absorbed separately.

The first wash-bottle was charged with concentrated sulphuric acid, which absorbed the nitrosyl chloride, producing hydrogen chloride and nitrosylsulphuric acid,



The mixture of hydrogen chloride and carbonyl chloride was then passed into bottles containing either benzene or toluene to absorb the carbonyl chloride. The hydrogen chloride was either allowed to escape, or in some experiments was collected in copper sulphate solution.

#### *Examination of the Sulphuric Acid Liquor.*

The contents of the first bottle had all the properties of a solution of nitrosylsulphuric acid in concentrated sulphuric acid. It did not, however, crystallise on long keeping in the ice-chest, even when the nitrosyl chloride had been passed through up to the limits of the capacity of the acid for efficient absorption. The liquor was therefore submitted to fractional distillation under diminished pressure. It was not possible to obtain a complete separation of the sulphuric acid from the nitrosylsulphuric acid, since some of the latter passed over even in the first runnings which, on keeping in the air for a short time, became distinctly blue. When about half

the acid had passed over, the sides of the receiver began to be coated with the well-known chamber crystals. On further distillation solid deposited in the condensing tube, the liquid in the receiver crystallised, and the residue in the distilling flask solidified on cooling.

This crystalline matter was purified, so far as possible, from free sulphuric acid by keeping it for many days on porous tile over sulphuric acid in a desiccator, and occasionally scraping on to fresh tile. In this way a quantity of approximately pure nitrosylsulphuric acid was obtained as a white, crystalline mass, which began to soften at about  $30^{\circ}$  with evolution of vapour. The crystals dissolved in a trace of water to a blue liquid, were readily soluble in concentrated sulphuric acid, and on dilution with much water gave a solution of sulphuric and nitric acid. The preparation contained no trace of chlorine.

A specimen was analysed by estimation of sulphuric acid after dissolving in water, and by titration of the solution in concentrated sulphuric acid into permanganate (Found,  $\text{SO}_3 = 63.86$ , oxygen required  $= 11.93$ ; Calc.,  $\text{SO}_3 = 63.01$ ; oxygen required  $= 12.59$  per cent.).

#### *Examination of the Benzene or Toluene Solutions.*

A toluene solution (114 c.c.), containing carbonyl chloride liberated in four days, was shaken with 150 c.c. of 40 per cent. potassium hydroxide solution in a closed bottle in the shaking machine for six hours. The alkaline layer was then made up to 250 c.c. Estimations of chloride and carbonate were made in this, and also in a control sample of potassium hydroxide, similarly treated.

- (1) 25 c.c. gave 2.6954 AgCl and 0.4487  $\text{CO}_2$ .
- (2) 25 c.c. ,, 2.6911 AgCl.
- (3) 26 c.c. control gave 0.0397 AgCl and 0.0372  $\text{CO}_2$ .

Ratio  $\text{Cl}:\text{CO}_2 = 1:0.6266$ .

Theory for  $\text{CoCl}_2 = 1:0.6205$ .

This toluene solution, from the rate of decomposition given below, should have contained between 8.4 and 11.2 grams of carbonyl chloride. It actually contained from the above analysis 9.16 grams.

In another experiment about 500 c.c. of benzene, containing the carbonyl chloride produced in forty-one days, were boiled in a flask with a reflux condenser, the upper end of which was connected to a worm condenser and receiver, both cooled by a freezing mixture of ice and salt, when between 7 and 8 c.c. of liquid carbonyl chloride, boiling at  $3^{\circ}$ , were obtained.

Much carbonyl chloride escaped condensation under these conditions, and a considerable amount remained in the benzene. The residual solution was shaken with concentrated aqueous ammonia and the aqueous layer evaporated to dryness. The crystallised residue was mainly ammonium chloride, but a trace of carbamide was isolated from it in the usual manner, and identified by its crystalline form, the biuret test, and the evolution of ammonia on treatment with soya-bean urease.

For the further identification of the carbonyl chloride it was converted into benzophenone by the Friedel and Crafts method. For this purpose about 250 c.c. of benzene, containing the carbonyl chloride evolved in seven to eight days, were used.

The benzophenone crystallised from alcohol in the usual characteristic form, and melted at  $48.5-49^{\circ}$ . A mixture with a specimen from another source showed no change in melting point. The yield was about 62 per cent. of the theoretical, and was similar in order to that recorded by Friedel and Crafts (*Ber.*, 1877, 10, 1856).

Dimethyl-*p*-aminobenzoic acid was also obtained, with other products, in needle-like crystals melting at  $235^{\circ}$ , by heating a toluene solution with dimethylaniline in a closed flask at  $130^{\circ}$  for several hours, and then distilling off the toluene in a current of steam.

#### *Examination of the Chloropicrin left after Prolonged Heating.*

This was yellow, and completely volatile in steam, leaving no residue. On distillation the following fractions were obtained: up to  $103^{\circ}$ , 3 grams;  $103-108^{\circ}$ , 5.2 grams;  $108-112^{\circ}$ , 278.7 grams; residue in flask, 3.8 grams. It was evidently unchanged chloropicrin.

The chloropicrin, after distillation in a current of steam, contained some nitrous fumes in solution, which were given off at the beginning of distillation and coloured the first fraction brown. These were easily displaced by a current of air.

Fraction 3 was found to contain Cl = 64.79, and two specimens of the commercial chloropicrin used 64.82 and 64.92 respectively.  $\text{CO}_2\text{NCl}_2$  requires Cl = 64.71 per cent.

#### *Rate of Decomposition.*

Chloropicrin (200 c.c.) was gently boiled for sixty-eight days, and 58 c.c. remained at the end. It decomposed therefore at the rate of 2.088 c.c. or 3.487 grams per day, and produced 2.099 grams of carbonyl chloride per day.

In another experiment in which the chloropicrin was kept rapidly

boiling, 64.6 grams of carbonyl chloride, determined from the increase in weight of the toluene wash-bottles, were obtained in twenty-three days, a rate of decomposition giving 2.8 grams per day.

In order to ascertain whether this decomposition could be attributed to traces of moisture, the chloropierin, which had been dried over calcium chloride and gave no reaction with anhydrous copper sulphate, was allowed to remain for several days with a large excess of phosphoric oxide. It was then transferred to the carefully dried apparatus and heated as described. Decomposition took place, and 8 grams of carbonyl chloride were obtained in ninety-one hours, a rate of decomposition giving 2.097 grams per day, and of much the same order as before. The residual chloropierin was found to contain Cl = 64.65 per cent.

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CIX.—*The Temperature of Critical Solution of a Ternary Mixture as a Criterion of Purity of n-Butyl Alcohol. The Preparation of Pure n-Butyl Alcohol.*

By KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES.

SINCE the introduction of the fermentation process, *n*-butyl alcohol prepared from starch has become a common industrial product which will certainly find a use in chemical industry and not improbably as a solvent.

We have examined some of its solubility relations with the object of finding in the temperature of critical solution ("c.s.t.") with other media a rapid and certain method of following the course of a fractionation by which butyl alcohol is being purified, or of detecting the presence of impurity in a specimen of butyl alcohol. It was pointed out in a previous paper (this vol., p. 1055), on a similar use of this method for toluene, that different impurities both present together in the liquid under investigation may have an opposite effect on the c.s.t. as on other physical properties. Usually, however, the c.s.t. of a number of fractions

into which the liquid has been divided by distillation will reveal the true condition of the liquid.

The solubility relations with water of the three isomerides of *n*-butyl alcohol have been studied by Alexéev (*Ann. Phys. Chem.*, 1886, [iii], **28**, 303) and Timmermans (*Zeitsch. physikal. Chem.*, 1907, **58**, 129).

*tert*-Butyl alcohol is miscible with water at the ordinary temperature, whilst the solubility curve of *isobutyl* alcohol has a c.s.t. at 130° (Alexéev), and *sec*-butyl alcohol one at 113.7° (Alexéev, Timmermans). Both curves show a maximum of mutual insolubility in the neighbourhood of 50°. The solubility curve of *n*-butyl alcohol has not been followed up to the c.s.t., which will be well above 150°, but it shows a similar maximum of insolubility at about 50°.

As a criterion of purity, the binary c.s.t. with water would not only be at an inconvenient temperature and pressure, but useless for detecting the commonest impurity, namely, water. No other binary mixture seems available, for although ethyl alcohol forms a binary with petroleum, which has found a similar application in Crismer's hands, and methyl alcohol with carbon disulphide, the higher alcohols are completely miscible with these liquids. A ternary mixture was therefore sought.

A 14 per cent. (13.994 grams per 100 grams of solution) solution of hydrochloric acid was chosen, as both very convenient for our purpose and sufficiently sensitive; it gives an upper c.s.t. at 43.55° and a lower at 9.6° with *n*-butyl alcohol.

*n*-Butyl alcohol is completely miscible with concentrated hydrochloric acid (20 per cent.) at the ordinary temperature (Lieben and Rossi, *Annalen*, 1871, **158**, 137). The presence of hydrochloric acid causes a contraction of the solubility ring of the system butyl alcohol-water, in the same way as does ethyl alcohol that of the system methyl ethyl ketone-water (Bruni, *Atti R. Accad. Lincei*, 1899, [v], **8**, 141).

Fig. 1 represents the change in the system *n*-butyl alcohol-water when hydrogen chloride is introduced. The solubility ring,  $KK'$ , of water and butyl alcohol has, as yet, been followed over only a small section of the lateral portions; the intervention of the solid-liquid curve,  $sl$ , prevents the realisation of the lower c.s.t.  $K'$ . When hydrogen chloride is present, the ring contracts;  $L'$ , the lower c.s.t., appears above the ice line, and  $L$ , the upper, is now at a lower temperature. As the concentration of the hydrogen chloride increases, the ring further contracts until, finally, miscibility is complete.



Aqueous sulphuric and nitric acids give upper ternary c.s.t.'s, but no lower c.s.t.'s were observed:

Sulphuric acid (24 per cent.) gave a c.s.t. at  $8^{\circ}$ , nitric acid (35 per cent.) at  $5^{\circ}$ .

Sulphuric acid (20 per cent.) gave a c.s.t. at  $80^{\circ}$ , nitric acid (31 per cent.) at  $37^{\circ}$ .

The method of determining the c.s.t., and the apparatus employed, have been fully described in an earlier paper (*loc. cit.*).

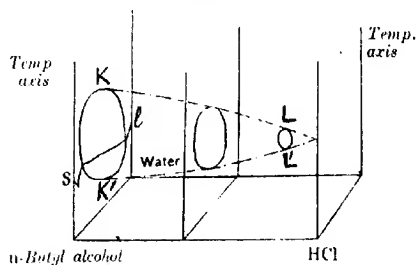
The quantities of the acid solution and butyl alcohol which gave very vividly the critical phenomena are:

Acid solution, 1 c.c.; butyl alcohol, 0.4958 c.c.

Pipettes of the type used for toluene were constructed and carefully calibrated to deliver these quantities with that exactness which we have shown (*loc. cit.*) to be so necessary.

*The n-Butyl Alcohol.*—In order to prepare a pure *n*-butyl

FIG. 1.



alcohol, several specimens from various sources have been examined. The untreated alcohols gave c.s.t.'s with the standard aqueous hydrochloric acid varying between such wide limits as an upper c.s.t. of  $84^{\circ}$  and complete miscibility, whereas pure butyl alcohol gives the value  $43.55^{\circ}$ .

Most of these crude alcohols, after treatment with ordinary chemical reagents—dilute acids to remove bases, sodium hydrogen sulphite to remove aldehydes and ketones, and boiling sodium hydroxide to decompose esters—and subsequent distillation, were found capable of giving a large percentage of material, the various fractions of which, on redistillation, gave the same c.s.t. about  $43^{\circ}$ . Some of the material, however, which was homogeneous so far as could be tested by distillation, gave c.s.t.'s varying widely from this value; as one example, the c.s.t. was about  $50^{\circ}$ , and as another about  $60^{\circ}$ .

As examples of the behaviour of these crude butyl alcohols on distillation, the following may be cited:

(1) A crude specimen (1000 c.c.) had an initial c.s.t. of 44.8°. After drying with potassium carbonate, the c.s.t. was reduced to 37.8°. On distillation through an eight-bulb still-head, the main fraction of 550 c.c., boiling at 116.5°, gave a c.s.t. of 46.8°.

After chemical treatment and redistillation, a considerable quantity of homogeneous material could be obtained from this main fraction (as well as from other specimens which had been similarly treated), the c.s.t. of which was 43–44°.

An alcohol (1000 c.c.) from another source, which was remarkable as being initially completely miscible with the standard hydrochloric acid, on mere distillation through an eight-column Young and Thomas dephlegmator furnished 750 c.c. of a homogeneous material giving a c.s.t. of 43°.

Two other examples may be mentioned of specimens which give after a similar treatment quite different values of the c.s.t.

Table I shows a record of fractionation of a specimen giving an initial c.s.t. of 66.7°.

TABLE I.

| Temperature. | Volume of distillate. | Critical point. | Temperature. | Volume of distillate. | Critical point. |
|--------------|-----------------------|-----------------|--------------|-----------------------|-----------------|
| 116.0°       | 10 c.c.               | 63.1°           | 116.3°       | 10 c.c.               | 61.5°           |
| 116.2        | 10 "                  | 61.7            | 116.4        | 10 "                  | 61.7            |
| 116.3        | 10 "                  | 59.8            | 116.4        | 10 "                  | 62.4            |
|              |                       |                 | 116.5        | 10 "                  | 64.6            |
|              |                       |                 | Residue.     | 7 "                   | above 90        |

Treatment with chemical reagents left the value of the c.s.t. unaltered.

The fractionation of another specimen, which gave after fractionation a homogeneous material with a c.s.t. of about 50°, is cited below (table II).

One was thus unable, in the absence of a pure synthetic alcohol, to decide definitely whether the homogeneous material, giving a c.s.t. of 43°, contained an impurity impossible to remove by distillation, which lowered the c.s.t., or whether the homogeneous material, giving a much higher c.s.t., contained impurities such as paraffins of similar boiling point, impossible to remove by distillation or chemical treatment, which raised the c.s.t.

It has been no simple matter to find a derivative of *n*-butyl alcohol which would provide a means of obtaining the pure substance. The derivative should preferably be a crystalline solid, into which the alcohol could be readily converted, and from which

V V\*

as readily recovered without chemical change of the alcohol. The sodium salt of butyl salicylate meets these conditions.

A large quantity of the alcohol, the fractionation of which is shown in the table (table II), was converted into the salicylate;

TABLE II.

| Fraction. | Volume. | Critical solution point. |
|-----------|---------|--------------------------|
| 1         | 40 c.c. | 57.0°                    |
| 2         | 252 "   | 50.0                     |
| 3         | 415 "   | 49.3                     |
| 4         | 295 "   | 49.0                     |
| 5         | 28 "    | 50.05                    |

the sodium salt is prepared by dropping the ester into a slight excess of 10 per cent. sodium hydroxide which is being vigorously stirred. The sodium salt crystallises out immediately; it is collected and freed from adherent liquor by pressure. The salt is reconverted into the ester by slowly adding both 10 per cent. hydrochloric acid and the solid salt to a large volume of cooled water which is being stirred. This process is repeated with the recovered ester. The ester is then hydrolysed by aqueous sodium hydroxide, and the butyl alcohol, saturated with water, is dried with potassium carbonate and distilled. Overheating, which would in itself lead to contamination, was avoided by using an oil-bath in this and other distillations. The table shows the values of the c.s.t.'s of the fractions in the final distillation.

TABLE III.

| Fraction. | Weight of fraction.<br>Grams. | Critical solution point. |
|-----------|-------------------------------|--------------------------|
| 1         | 10                            | 43.7°                    |
| 2         | 27                            | 43.55                    |
| 3         | 27                            | 43.55                    |
| 4         | 30                            | 43.5                     |
| 5         | 20                            | 43.5                     |
| Residue   | about 5                       | -                        |

It is seen that the material is now remarkably homogeneous. This *n*-butyl alcohol, which gives an upper c.s.t. at 43.55° and a lower c.s.t. at 9.6° with 13.994 per cent. hydrochloric acid, has  $D_{44}^{20}$  0.81617.

*Relation Between the Concentration of Hydrochloric Acid and the Ternary Critical Solution Temperatures observed with n-Butyl Alcohol.*

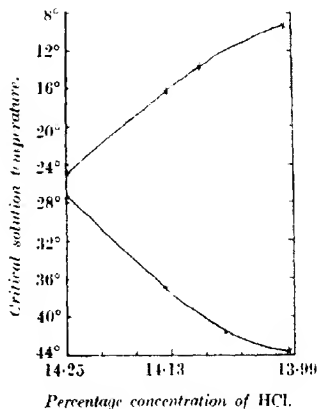
The c.s.t. is extremely sensitive to change in the concentration of the hydrogen chloride. Hydrochloric acid solutions of various

strengths were made up, and a definite volume (1 c.c.) was added to a definite volume of *n*-butyl alcohol (0.4958 c.c.) in the experimental tube. The table shows the experimental values, and Fig. 2 the curves constructed from them.

TABLE IV.

| Concentration of acid.<br>(grams in 100 grams of solution.) | Critical solution points. |        |
|---|---------------------------|--------|
|   | Upper.                    | Lower. |
| 13.994  | 43.55°                    | 9.6°   |
| 14.068  | 41.8                      | 12.1   |
| 14.133  | 36.8                      | 16.3   |
| 14.248  | 27.4                      | 25.0   |

FIG. 2.



So small a change in the concentration of the hydrochloric acid as 0.254 per cent. alters the upper c.s.t. by 16.15°, and the lower by 15.4°. This great sensitiveness would afford a means of ascertaining whether two solutions of hydrochloric acid within a small range were of accurately identical concentration.

The measurement of the concentration of the hydrochloric acid solution has required exceptional care. As the most accurate process, a determination was chosen based on the measurements of the iodine (by *N*/20-thiosulphate, and starch indicator), set free from a mixture of potassium iodide and iodate, in which the amount of iodate is very accurately known. (Fuller details of the procedure will appear, it is hoped, in another place.) This method has been fully tested, and the accuracy with which

the solution of hydrochloric acid has been measured is represented by the number  $14.248 \pm 0.001$  per cent. This mean error corresponds with a difference of  $0.05^\circ$  in the c.s.t. of the system *n*-butyl alcohol–water–hydrochloric acid. This particular solution of hydrochloric acid was used throughout the experiments on the purification of *n*-butyl alcohol.

Obviously, in preparing an aqueous hydrochloric acid for the purpose of following the purification of *n*-butyl alcohol, the concentration of the hydrochloric acid used need not be known with such accuracy. With the ordinary volumetric solutions, accurately standardised, and by using standard burettes, the concentration of the hydrochloric acid can be ascertained as  $14.0 \pm 0.02$  per cent., and by a gravimetric analysis as  $14.0 \pm 0.005$  per cent. The divergence in the c.s.t. corresponding with this mean error will amount to  $1^\circ$  in the one and to  $0.25^\circ$  in the other.

*The Sensitiveness of the Critical Solution Temperature to Impurities.*

*Water.*—Water is one of the components of the system, and its effect as an impurity in the *n*-butyl alcohol is seen from table V to be comparatively slight; 1 per cent. of water raises the upper c.s.t. by  $1^\circ$ . Here, as in all these experiments on the effects of impurities, the concentration of the hydrogen chloride remains constant, the composition of the system only altering in the relative proportions of *n*-butyl alcohol and water. The immensely different effect produced when the concentration of the *n*-butyl alcohol remains constant, while the ratio  $\frac{\text{concentration of HCl}}{\text{concentration of H}_2\text{O}}$  is varied, is seen from the results on the relation between the concentration of the hydrochloric acid and the c.s.t., when a change of  $0.25$  per cent. leads to a fall or rise in the c.s.t. of  $16^\circ$ .

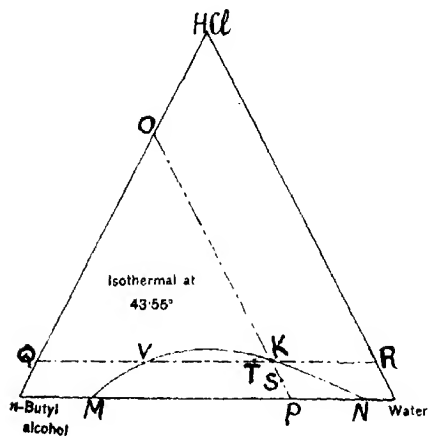
An explanation of this divergence is forthcoming from a consideration of the isothermal diagram at  $43.55^\circ$ .

In Fig. 3, *M* (80 per cent. of butyl alcohol) and *N* (8 per cent. of butyl alcohol) represent, roughly, the composition of a saturated solution of water in *n*-butyl alcohol and of alcohol in water at this temperature. *K* represents the composition of the system at the ternary c.s.t. at  $43.55^\circ$ . ( $\text{HCl} = 10.15$ ; *n*-butyl alcohol = 27.45; water = 62.4 per cent.)

From these results, it appears that the binodal curve has the general form shown—a curve with a very flat top. The line *OKP* represents the composition of the system with constant concentration of *n*-butyl alcohol, and the line *QKR* the composition of

the system with constant concentration of hydrochloric acid. From  $K$ , movement along  $KSP$ , that is, decrease in the concentration of the hydrochloric acid, with a corresponding increase in the concentration of water, the concentration of the alcohol being constant, brings the system into the heterogeneous region; by movement along  $KTQ$ , that is, decrease in the concentration of water, with a corresponding increase in the concentration of the alcohol, the concentration of the hydrochloric acid being constant, the system is brought again into the heterogeneous region, but at

FIG. 3.



no point is it far removed from the binodal curve, which it again cuts at  $V$ .

Let  $KT$  represent a 1 per cent. change in the ratio  $\frac{n\text{-butyl alcohol}}{\text{water}}$ , the concentration of the hydrochloric acid being constant, then  $KS$ , which equals  $KT$ , represents a 1 per cent. change in the ratio  $\frac{\text{hydrochloric acid}}{\text{water}}$ , the concentration of the

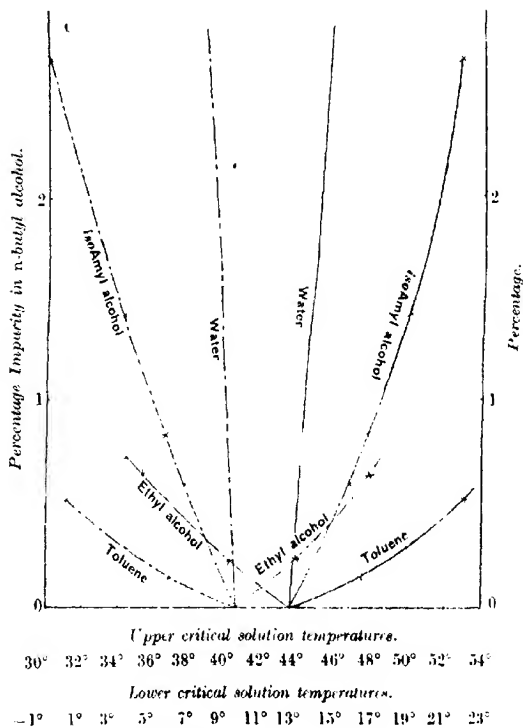
alcohol being constant.  $S$  is obviously very much further removed from the binodal surface than  $T$ . Hence, as a result of the form of the binodal curves, a far larger change of temperature would be required to bring the system at  $S$  on to a binodal curve than the system at  $T$  on to a curve.

The results obtained with the other substances, namely, toluene,

ethyl alcohol, and amyl alcohol, which have been tested, appear in table V and Fig. 4.

The c.s.t. is extremely sensitive to the presence of such a substance as toluene, the solubility of which in water so greatly differs from that of *n*-butyl alcohol. One per cent. of toluene in the butyl alcohol raises the upper and depresses the lower c.s.t. by 19°.

FIG. 4.



The c.s.t. is thoroughly sensitive to the presence of homologues. One per cent. of ethyl alcohol lowers the upper c.s.t. by 11°, and 1 per cent. of amyl alcohol raises the upper c.s.t. by 5°, correspond-

ing alterations being observed in the lower c.s.t. Rough experiments with *n*-propyl, *isobutyl*, and *sec.*-butyl alcohols show a less, but still an appreciable, effect. One per cent. of *n*-propyl alcohol lowers the c.s.t. by 6.1°, 1 per cent. of *isobutyl* alcohol by 0.7°, and 1 per cent. of *sec.*-butyl alcohol by 1.9°. The relations of the c.s.t.'s of isomerides are being more fully examined.

The values of the c.s.t. in table V were obtained when the quantities of the two constituents delivered respectively by the two pipettes were used, that is, 1 c.c. of the standard hydrochloric acid and 0.4958 c.c. of impure *n*-butyl alcohol. The "percentage" of admixture is by weight in the *n*-butyl alcohol.

TABLE V.

|                                  |        |        |        |        |        |
|----------------------------------|--------|--------|--------|--------|--------|
| Water present, per cent.         | 0      | 2.677  | 2.796  | 10.75  | 4.034  |
| Upper c.s.t. ....                | 43.55° | 45.7°  | 46.2°  | 52.35° | 47.95° |
| Lower c.s.t. ....                | 9.6    | 8.2    | 7.9    | 3.0    | 6.5    |
| Toluene present, per cent.       | 0      | 0.1422 | 0.3157 | 0.5077 |        |
| Upper c.s.t. ....                | 43.55° | 47.4°  | 50.1°  | 53.2°  |        |
| Lower c.s.t. ....                | 9.6    | 5.8    | 3.15   | -1.15  |        |
| Amyl alcohol present, per cent.  | 0      | 0.5910 | 0.8366 | 2.466  | 1.413  |
| Upper c.s.t. ....                | 43.55° | 46.95° | 47.6°  | 53.8°  | 50.1°  |
| Lower c.s.t. ....                | 9.6    | 6.75   | 5.8    | -0.9   | 3.25   |
| Ethyl alcohol present, per cent. | 0      | 0.6288 | 0.2381 |        |        |
| Upper c.s.t. ....                | 43.55° | 35.3°  | 40.1°  |        |        |
| Lower c.s.t. ....                | 9.6    | 16.8   | 12.8   |        |        |

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### CX.—The Action of Grignard Reagents on the Esters of Certain Dicarboxylic Acids.

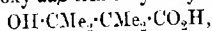
By HARRY HEPWORTH.

THE action of Grignard reagents on the esters of the simpler saturated aliphatic dicarboxylic acids has been the subject of several investigations. Valeur (*Compt. rend.*, 1901, **132**, 833) obtained ditertiary glycols by the action of magnesium methyl iodide and magnesium ethyl iodide on ethyl oxalate, ethyl malonate, and ethyl succinate, and somewhat later (*Compt. rend.*, 1903, **136**, 694) prepared benzopinacolone and tetraphenylbutanediol by the



action of magnesium phenyl bromide on methyl oxalate and ethyl succinate respectively. Dilthey and Last (*Ber.*, 1904, **37**, 2639) claimed to have prepared  $\beta$ -benzopinacolin from ethyl oxalate, and magnesium phenyl bromide, and diphenylphenacylcarbinol,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$ , from ethyl succinate in a similar way. Valeur, however, still claimed that the product of the action of magnesium phenyl bromide on methyl or ethyl oxalate is benzopinacolone (*Compt. rend.*, 1904, **139**, 480). Again, Harries (*Annalen*, 1905, **343**, 363) prepared  $\beta$ -dimethylhexane- $\beta$ -diol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ , by the interaction of magnesium methyl iodide and ethyl succinate. In all these investigations the experimental conditions have been such as would favour attack on both carboxyalkyl groups by the Grignard compound employed, with the result that almost invariably fully substituted glycols or compounds of an analogous nature have been produced.

An exception arises in the work of Slavjanov (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 140), who, during the course of some experiments on the preparation of hexamethylcyclopropane, incidentally obtained some  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyric acid,



by the action of magnesium methyl iodide on methyl dimethylmalonate. The only other evidence of selective action of Grignard reagents on one of the two carboxyalkyl groups of the esters of the simpler aliphatic dicarboxylic acids appears to be that of Egorova (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1454), who acted on ethyl oxalate with magnesium *tert*-butyl chloride, and obtained, amongst other products,  $\alpha$ -hydroxy- $\beta\beta$ -dimethylbutyric acid,  $\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , and  $\alpha$ -ethoxy- $\beta\beta$ -dimethylbutyric acid,  $\text{CMe}_2\cdot\text{CH}(\text{OEt})\cdot\text{CO}_2\text{H}$ ; whilst, in the hope of finding a convenient method of obtaining  $\alpha$ -ketonic acids, the action of Grignard reagents on ethyl oxalate was investigated by Inglis and Mason (*P.*, 1909, **25**, 195), but the work described in this note is incomplete and does not appear to have been subsequently published.

In view of the fact that the discrepancy between the observations of Slavjanov (*loc. cit.*) and the results of other workers might be attributed either to a form of steric hindrance exerted by the methyl-substituting groups of the ester of dimethylmalonic acid or to the fact that Slavjanov used only three equivalents of magnesium and methyl iodide, whereas Valeur, Dilthey, and Harries used at least four equivalents, it was decided to carry out experiments to ascertain whether, by suitable control, the action of the Grignard reagent on the esters of certain aliphatic dicarboxylic acids could be confined to one carboxyalkyl group.

In this connection, it is interesting to note that Grignard

reagents react in a rather anomalous and unexpected manner with ethyl acetoacetate and its alkyl derivatives. Thus Grignard has shown (*Compt. rend.*, 1902, **134**, 849) that magnesium methyl iodide and ethyl acetoacetate give methane, hydrogen, and unchanged ester, the ester thus reacting in the enolic form. On the other hand, the monoethyl derivative of ethyl acetoacetate and magnesium methyl iodide react to give some ethyl  $\beta$ -hydroxy- $\alpha$ -ethylisovalerate,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ , whilst methyl diethylacetoacetate does not react at all. Again, McKenzie (*T.*, 1906, **89**, 380) has shown that menthyl acetoacetate reacts as though entirely enolic.

Experiments have been carried out on the action of magnesium methyl iodide and magnesium ethyl bromide on ethyl oxalate, ethyl malonate, ethyl ethylmalonate, ethyl dimethylmalonate, and ethyl succinate, using about 2.5 equivalents of magnesium and alkyl haloids to one of ester. With the exception of ethyl malonate, which appears to react entirely in the enolic form, the reaction has been so regulated as to confine the action of the Grignard compound almost completely to one carboxyalkyl group.

In these experiments it was not found necessary to prepare the Grignard reagent separately, as the best results were obtained by dropping a mixture of alkyl haloid and ester into a well-stirred and cooled mixture of magnesium powder and dry ether (compare Davies and Kipping, *T.*, 1911, **99**, 296). The mixture of alkyl haloid and ester was added at such a rate as to keep the reaction just perceptibly in progress.

In this way  $\alpha$ -hydroxyisobutyric acid and  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid were prepared from ethyl oxalate,  $\beta$ -hydroxy- $\alpha$ -ethylisovaleric acid from ethyl ethylmalonate,  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyric acid from ethyl dimethylmalonate, and isohexolactone and  $\gamma$ -ethyl-*n*-hexolactone from ethyl succinate.

Now Shibata has shown (*T.*, 1909, **95**, 1449) that Grignard reagents react with ortho-phthalic esters to give derivatives of phthalide, in which only one carboxyalkyl group of the phthalic ester is attacked. He compares this reaction with the production of tetra-alkylbutanediols from ethyl succinate and Grignard compounds (Valeur, *loc. cit.*), and concludes from this, together with the work of Bethmann (*Zeitsch. physikal. Chem.*, 1890, **5**, 409) on succinic acid, that in the latter compounds the two carboxyl groups are in the *trans*-position, whereas in *o*-phthalic acid the carboxyl groups are in the *cis* position. It has now been shown that the action of the Grignard compound may be confined to one carboxyalkyl group in the case of ethyl succinate with the production of  $\gamma$ -dialkylbutyrolactones, from which it might equally well be

concluded that the two carboxyl groups in succinic acid are in the *cis*-position. All that can be safely inferred, however, seems to be that in the intermediate compounds obtained by the interaction of Grignard compounds and ethyl succinate or orthophthalic esters, the hydroxyl and carboxyalkyl groups are possibly in the *cis*-position, and in the absence of any strictly quantitative data it is somewhat hazardous to draw any conclusions as to the steric structures of succinic and phthalic acids from such observations.

#### EXPERIMENTAL.

##### *Preparation of $\alpha$ -Hydroxy- $\alpha$ -ethylbutyric Acid from Ethyl Oxalate.*

Three hundred grams of dry ether and 10 grams of magnesium powder were introduced into a wide-necked flask provided with a stirrer, dropping funnel, and condenser, and surrounded by ice. Ten grams of ethyl bromide were placed in the flask, and after the reaction had started a mixture of 73 grams of ethyl oxalate and 126 grams (2.5 mols.) of ethyl bromide was added at such a rate as to keep the reaction proceeding slowly. The rest of the magnesium, 21 grams (2.5 mols.), was added from time to time so as to keep the magnesium always in excess. Towards the end of the reaction the contents of the flask became very viscous. Stirring was continued for an hour after the whole of the magnesium had been added, after which the mixture was allowed to remain overnight at the ordinary temperature.

The mixture was then heated on a water-bath for two hours and, after cooling, ice-cold water followed by 40 per cent. sulphuric acid was slowly added until the whole of the magnesium had dissolved.

A brown oil separated, and after its removal the residue was extracted four times with ether. The oil and ethereal extract were combined, dried over anhydrous sodium sulphate, and the ether removed by distillation, when 61 grams of a brown, rather viscous oil remained.

This oil was then distilled, when about 53 grams passed over between 172° and 185°. At 210° there was evidence of decomposition and the distillation was stopped. The fraction distilling at 172—185° was fractionated in a five-pear column, when about 48 grams distilled at 174—180° and about 4 grams at 180—186°. The latter proved to be principally unchanged ethyl oxalate.

The fraction distilling at 174—180° was redistilled, when 45.5 grams (57 per cent.) of ethyl  $\alpha$ -hydroxy- $\alpha$ -ethylbutyrate distilled at 175—177° (corr.) (Frankland and Duppa, *Annalen*, 1863, 126, 109).

Sixteen grams of the ester were boiled under reflux with 5 grams

(1½ mols.) of sodium hydroxide for two hours. After cooling and acidifying, a solid separated, which was removed, and the residue extracted six times with ether. There were obtained 12 grams of an acid, which crystallised from light petroleum in long needles melting at 79.5°.

The identity of this acid with  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid was established by conversion into its barium salt (Found, Ba=34.22; calc., Ba=34.3 per cent.) and by its conversion into the ethylisocrotonic acids on repeated distillation (Fittig, *Annalen*, 1904, **334**, 101).

*Preparation of  $\alpha$ -Hydroxyisobutyric Acid from Ethyl Oxalate.*

This was carried out on exactly the same lines as the preparation of  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid described above, except that methyl iodide was used instead of ethyl bromide. Seventy-three grams of ethyl oxalate were treated with 30 grams (2.5 mols.) of magnesium powder and 180 grams (2.5 mols.) of methyl iodide; 39.6 grams (60 per cent.) of an oil boiling at 150–151° were obtained, and the identity of this with ethyl  $\alpha$ -hydroxyisobutyrate was confirmed by conversion of 10 grams of the ester into the acid. The latter melted at 78° and the barium salt was analysed (Found, Ba=39.82; calc., Ba=39.98 per cent.) (Frankland and Duppa, *Annalen*, 1865, **133**, 80; Fittig, *ibid.*, 1877, **188**, 54).

Several attempts were made to increase these yields by variations in the addition of the reagents, but in no case was a yield greater than 60 per cent. obtained. Unless the addition of alkyl haloid and ester is made very slowly, a considerable amount of a by-product, which is probably a butanediol, is formed.

*Preparation of  $\gamma$ -Ethyl- $\alpha$ -hexolactone from Ethyl Succinate.*

Eighty-seven grams of diethyl succinate (b. p. 215–216°) were treated with 30 grams (2.5 mols.) of magnesium powder and 136 grams (2.5 mols.) of ethyl bromide in 400 c.c. of dry ether as described in the preparation of ethyl  $\alpha$ -hydroxy- $\alpha$ -ethylbutyrate. After removal of the ether, an oil was obtained, of which the greater part distilled at 125–140°/23 mm., although a little passed over at 120–123°. The former fraction, weighing 32 grams, was fractionated under the ordinary pressure, when 26 grams distilled at 227–232° (corr.). This fraction was freed from any unchanged ethyl succinate by boiling under reflux with 15 grams of sodium hydroxide for two hours, acidifying with concentrated hydrochloric acid, and boiling for a further half-hour, when an oil separated

on the surface. This was removed and the residue extracted eight times with ether. The oil and ethereal extract were then combined and washed with a little sodium carbonate to remove succinic acid. After removal of the ether, 27 grams of an oil remained, which on redistillation boiled at 229--231° (corr.).

A further 6 grams of the lactone were obtained by working up the fraction distilling at 120--123°/23 mm. The total yield was 33 grams (46 per cent. of the theoretical).

The identity of this compound with  $\gamma$ -ethyl-*n*-hexolactone was established by its conversion into the barium salt of  $\gamma$ -hydroxy- $\gamma$ -ethyl-*n*-hexoic acid (Wischen, *Annalen*, 1867, **148**, 262; Emmert, *Ber.*, 1888, **15**, 1851). The latter was obtained as an amorphous powder, readily soluble in water or alcohol, which on recrystallisation from alcohol gave Ba=30.12 (calc., Ba=30.17 per cent.).

*Preparation of isohexolactone from Ethyl Succinate.*

Eighty-seven grams of diethyl succinate were treated with 30 grams (2.5 mols.) of magnesium and 177 grams (2.5 mols.) of methyl iodide exactly as described above. An oil (57 grams: 50 per cent. of the theoretical) was eventually obtained which boiled at 200--202° (Blanc, *Compt. rend.*, 1904, **138**, 579; **139**, 65). The identity of this with isohexolactone was established by conversion into the barium salt of  $\gamma$ -hydroxyisohexoic acid (Found, Ba=34.3; calc., Ba=34.3 per cent.).

Experiments were carried out in which the whole of the ethyl succinate was placed in the flask and the ethyl bromide slowly added, but the reaction was more difficult to control and no greater yield was obtained.

*Action of Magnesium Methyl Iodide on Ethyl Malonate.*

A mixture of 16 grams of ethyl malonate (b. p. 198°) and 36 grams of methyl iodide (2.5 mols.) was added drop by drop to 6 grams of magnesium in 100 c.c. of dry ether as described under the preparation of  $\alpha$ -hydroxy- $\alpha$ -ethylbutyric acid from ethyl oxalate. On decomposing the product with water and dilute sulphuric acid, the greater part of the ethyl malonate was recovered unchanged. From this it would appear that under these conditions ethyl malonate reacts in the enolic form.

*Action of Magnesium Methyl Iodide on Ethyl Ethylmalonate.*

A mixture of 19 grams of ethyl ethylmalonate (b. p. 204--206°) and 36 grams of methyl iodide (2.5 mols.) was added drop by drop

to a well-cooled and stirred mixture of 6 grains of magnesium and 100 c.c. of dry ether as described before. The mixture was allowed to remain overnight at the ordinary temperature and then heated under reflux, on a water-bath, for three hours.

After decomposing, an oil was obtained, the greater part of which distilled at 200–207° and proved to be ethyl ethylmalonate. About 5 grams of a fraction of higher boiling point (220–240°) was collected, and on hydrolysis gave an acid which, when crystallised from light petroleum containing a little acetone, melted at 72°. This acid appeared to be  $\beta$ -hydroxy- $\alpha$ -ethylisovaleric acid, obtained by Grignard (*Compt. rend.*, 1902, **134**, 849) by the action of magnesium methyl iodide on ethyl ethylacetoacetate. The barium salt on analysis gave Ba = 32.07 (calc., Ba = 32.11 per cent.)

*Action of Magnesium Methyl Iodide on Ethyl Dimethylmalonate.*

Slavjanov (*loc. cit.*) obtained  $\beta\delta$ -dihydroxy- $\beta\gamma\gamma\delta$ -tetramethylpentane and  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyric acid by heating one equivalent of ethyl dimethylmalonate with three equivalents of magnesium and methyl iodide in the presence of dry ether, on a water-bath for three to five hours.

A mixture of 19 grams of ethyl dimethylmalonate and 36 grams of methyl iodide (2.5 mols.) was added drop by drop to a well-cooled and stirred mixture of 6 grams of magnesium in 100 c.c. of dry ether, as described before. The mixture was allowed to remain overnight at the ordinary temperature, and then heated under reflux on a water-bath for three hours.

After decomposing, an oil separated which on distillation gave a fraction (9 grams) boiling at 190–210° and a second fraction (7 grams) boiling at 220–250°. The former proved to be ethyl dimethylmalonate, whilst the latter, on hydrolysis, gave an acid which on purifying by sublimation melted at 151–152°. This acid appeared to be identical with  $\beta$ -hydroxy- $\alpha\alpha\beta$ -trimethylbutyric acid first prepared by Reformatsky (*Ber.*, 1895, **28**, 2839). During the hydrolysis of the fraction boiling at 220–250° a little insoluble material remained, which on recrystallisation melted at 77°. This was probably  $\beta\delta$ -dihydroxy- $\beta\gamma\gamma\delta$ -tetramethylpentane, but there was insufficient material for further examination.

Preliminary experiments on this investigation were carried out at University College, Nottingham, in 1915, under the direction of Prof. Kipping.

The author is indebted to the Research Committee of Messrs.

Nobel's Explosives Co., Ltd., and particularly to Mr. Rintoul, for the facilities accorded him for the completion of this work, and also to Mr. Carr, of Messrs. Boots, Ltd., for permission to publish certain portions of this investigation.

THE RESEARCH LABORATORIES,  
ARDEER.

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### (Xl.—*The Melting Points of the Substituted Amides of the Normal Fatty Acids.*

By PHILIP WILFRED ROBERTSON.

OUR knowledge of the physical properties of homologous series is largely due to the researches of Krafft. Whereas the densities approximate to a constant value as the series is ascended, the melting points and boiling points continue to rise, although the successive differences become smaller and smaller. To this general rule, however, the normal fatty acids form a noteworthy exception, since their melting points fall to a minimum and then subsequently rise, and further since the values for the odd and the even members fall on two distinct curves. This exceptional behaviour has been attributed to the association of the earlier members of the series, which itself is probably not unconnected with the arrangement of the atoms in space. Some years ago it was pointed out (Robertson, T., 1908, 93, 1033) that the amides, anilides, and *p*-toluidides showed an even greater irregularity, which was explained, rather vaguely, as being due to molecular dissymmetry. In the hope of obtaining a nearer insight into the relationship between melting point and chemical composition, certain new series, in particular, bromo-derivatives, have now been investigated. In the meantime a systematic search through the earlier and more recent literature had revealed a considerable discrepancy between the values published by different observers; in some cases the melting points given for a compound differed by as much as 20°. In these circumstances it was felt necessary to make a complete redetermination of the melting points of these series. The correctness of a given melting point would appear to depend essentially on the following factors: (a) the identity of the normal fatty acid employed in the preparation, (b) its purity, and especially its freedom from neighbouring homologues, which in the final product can be separated often only with the greatest difficulty; (c) the purity of the product (especially when it is very readily soluble and tends to separate as an oil).

which was attained by numerous recrystallisations from different solvents; (d) the accuracy of the melting point determination. As is indicated in the sequel, every effort has been made to fulfil these conditions.

The melting points of the amides, anilides, *p*-toluidides, *o*-toluidides, *p*-bromoanilides, *o*-bromo-*p*-toluidides, tribromo-anilides,  $\beta$ -naphthylamides, and  $\alpha$ -bromo- $\beta$ -naphthylamides are collected in the following tables. Each series will first of all be considered separately and then the results will be discussed as a whole.

TABLE I.

| No. of carbon<br>atoms in chain. | Amides. |     | Anilides. |      | <i>p</i> -Toluidides. |     |
|----------------------------------|---------|-----|-----------|------|-----------------------|-----|
|                                  | M. p.   |     | M. p.     |      | M. p.                 |     |
| 2                                | 82°     | 77° | 112°      | 106° | 153°                  | 126 |
| 4                                | 115     | 106 | 96        | 63   | 75                    | 74  |
| 6                                | 101     | 96  | 92        | 65   | 73                    | 80  |
| 8                                | 105     | 99  | 55        | 57   | 70                    | 84  |
| 10                               | 99      | 99  | 70        | 71   | 78                    | 80  |
| 12                               | 100     | 99  | 78        | 80   | 87                    | 88  |
| 14                               | 103     | 100 | 84        | —    | 93                    | —   |
| 16                               | 106     | —   | 89        | —    | 98                    | —   |
| 18                               | 109     | —   | 94        | —    | 102                   | —   |

*Amides* (Table I; Fig. 1).

As is clearly visible in the figure, the melting points of the odd and even members fall on two distinct curves, which, although not superposable, rise and fall in the same manner at corresponding places. The initial rise is characteristic only of the amides; the substituted amides, and the fatty acids also, show a fall in melting point at the beginning of the series. It is to be noted that the lower fatty amides, like the corresponding acids, are considerably associated; but the type of melting-point curve is quite different in the two series.

*Anilides* (Table I; Fig. 2).

The melting points of the even anilides fall to a sharp minimum at the eighth member, with a noticeable flattening between the fourth and sixth members. The large fall in melting point between the  $C_6$  and the  $C_8$  anilide, no less than 37°, is very remarkable.



FIG. 1.

*Amides.*

(Even members ———; odd members - - - -)

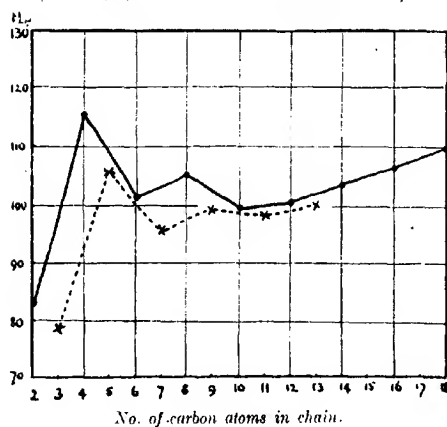
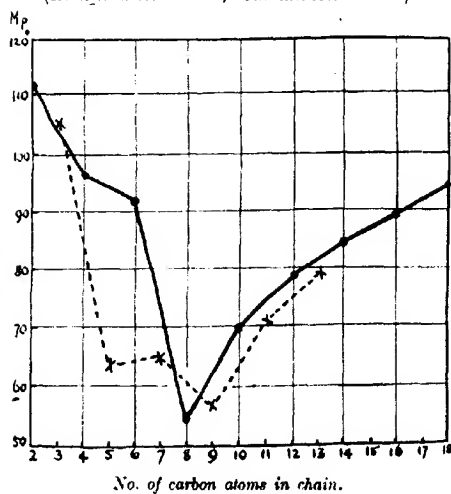


FIG. 2.

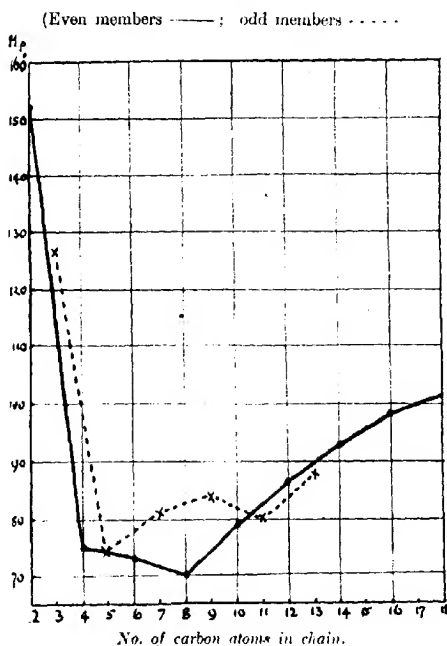
*Amidides.*

(Even members ———; odd members - - - -)



The odd series shows a similar large fall followed by a slight rise at the fifth member, corresponding with the flattening in the even series. It is to be noticed that this curve is, at the beginning, exactly the reverse of the odd curve of the amides. The factor causing the irregularity apparently is acting in the reverse sense in

FIG. 3.

*p-Toluidides.*

two series until its effect is eliminated by another factor, some function of the molecular weight, which begins to operate higher in the series.

*p-Toluidides* (Table I; Fig. 3).

The introduction of a methyl group in the para-position of the amide causes a fundamental change in the melting-point relationships. In the even series the noticeably large initial fall is followed by a very slow decrease to the minimum at the eighth member.

In the odd series, on the other hand, the initial fall is followed by a slight rise and subsequent fall to a second minimum at the eleventh member.

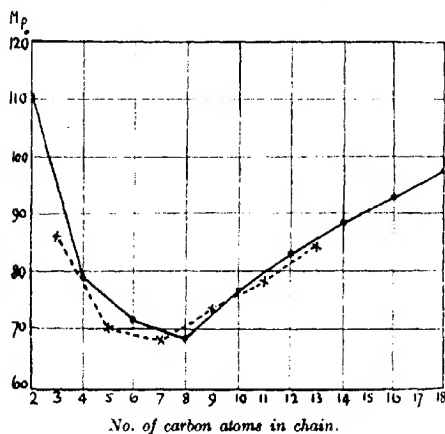
TABLE II.

| No. of carbon atoms in chain. | <i>o</i> -Toluidides. | <i>o</i> -Bromo- <i>p</i> -toluidides. | <i>p</i> -Bromo-anilides. |
|-------------------------------|-----------------------|--|---------------------------|
|                               | M. p.                 | M. p.                                  | M. p.                     |
| 2                             | 110°                  | 118°                                   | 167°                      |
| 3                             | 87                    | 111°                                   | 149°                      |
| 4                             | 79                    | 90                                     | 115                       |
| 5                             | 70                    | 100                                    | 108                       |
| 6                             | 71                    | 84                                     | 105                       |
| 7                             | 68                    | 90                                     | 98                        |
| 8                             | 69                    | 78                                     | 103                       |
| 9                             | 73                    | 86                                     | 100                       |
| 10                            | 76                    | 82                                     | 102                       |
| 11                            | 78                    | 91                                     | 102                       |
| 12                            | 83                    | 85                                     | 104                       |
| 13                            | 85                    | 95                                     | —                         |
| 14                            | 88                    | 89                                     | 107                       |
| 15                            | —                     | —                                      | —                         |
| 16                            | —                     | —                                      | 110                       |
| 17                            | —                     | —                                      | —                         |
| 18                            | 97                    | 97                                     | 114                       |

FIG. 4.

*o*-Toluidides.

(Even members —; odd\* members - - -)

*o*-Toluidides (Table II; Fig. 4).

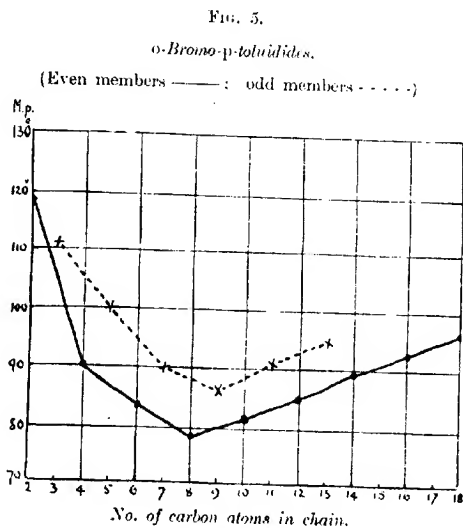
Both the odd and even members form the typical curve, that is, the melting points fall to a minimum and then rise again with increasing slowness as the series is ascended.

In Figs. 1 to 4 it is seen that after the eleventh member the melting points of the odd compounds fall slightly below the even values, which behaviour characterises the fatty acids also. This appears to be the general rule, to which the next series is, however, an exception.

*o*-Bromo-*p*-toluidides (Table II; Fig. 5).

The even and the odd series form typical curves, approximately parallel to each other.

Whereas the odd melting points generally tend to coincide with or fall slightly below the even values, at all events with compounds



of high molecular weight, here their average melting point is no less than 6° higher. It has not been found possible to correlate this noticeable difference in behaviour with any other characteristic of the series.

*p*-Bromo-anilides (Table II; Fig. 7).

As is seen in Fig. 7, in which the melting points of the even series only are plotted, there is a large fall from the second to the fourth member, followed by a further slow fall to a minimum at the C<sub>10</sub> compound. The odd values fall somewhat below the even and show a minimum at the seventh member.

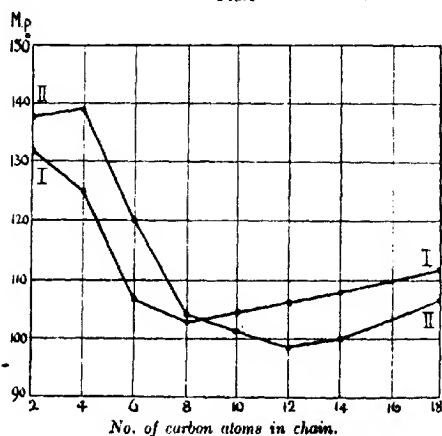
TABLE III.

| No. of carbon atoms in chain. | 2:4:6-Tri-bromo-anilides.<br>M. p. | $\beta$ -Naphthyl-anilides.<br>M. p. | $\alpha$ -Bromo- $\beta$ -naphthylamides.<br>M. p. |
|-------------------------------|------------------------------------|--------------------------------------|--|
| 2                             | 232°                               | 132°                                 | 138°   |
| 3                             | 203°                               | —                                    | 139°   |
| 4                             | 179                                | 125                                  | 139  |
| 5                             | —                                  | 112°                                 | 136  |
| 6                             | 136                                | 107                                  | 120  |
| 7                             | 134                                | 101                                  | 111  |
| 8                             | 131                                | 103                                  | 104  |
| 9                             | 131                                | 103                                  | 103  |
| 10                            | 129                                | 104                                  | 102  |
| 11                            | 129                                | —                                    | —  |
| 12                            | 126                                | 106                                  | 99   |
| 13                            | —                                  | 107                                  | —  |
| 14                            | 124                                | 108                                  | 100  |
| 15                            | —                                  | —                                    | —  |
| 16                            | 124                                | —                                    | —  |
| 17                            | —                                  | —                                    | —  |
| 18                            | 126                                | 112                                  | 106  |

2:4:6-Tribromo-anilides (Table III; Fig. 7).

The rapid initial fall in melting point noticed in the  $\mu$ -bromo-anilides becomes in this series even more exaggerated, and the minimum is now higher in the series. The curve for the odd members is almost coincident with the even curve.

FIG. 6

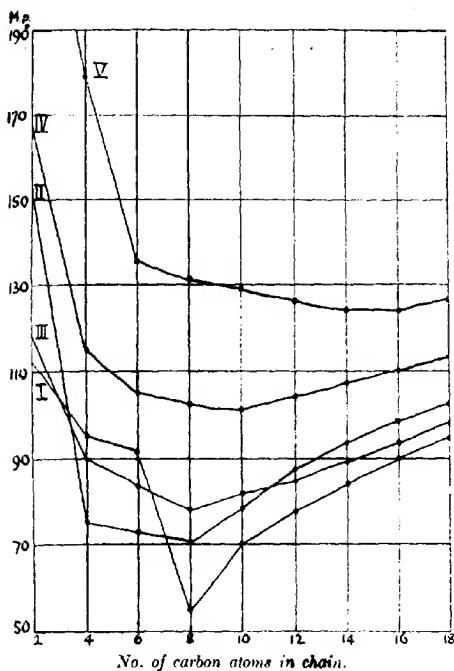


I.  $\beta$ -Naphthylamides. II.  $\alpha$ -Bromo- $\beta$ -naphthylamides.

*$\beta$ -Naphthylamides* (Table III; Fig. 6).

The comparatively slow initial fall in melting point differentiates this series from those hitherto considered. The curve for the odd members at first falls slightly below and then coincides with the even curve.

FIG. 7.



I. Anilides. II. p-Toluidides. III. o-Bromo-p-toluidides.  
IV. p-Bromo-anilides. V. Tribromo-anilides.

 *$\alpha$ -Bromo- $\beta$ -naphthylamides* (Table III; Fig. 6).

The effect of introducing a bromine atom is to change the initial low fall in melting point of the  $\beta$ -naphthylamides into a very slight rise, and to cause the minimum to occur higher in the series. The curves for the odd and even members tend to coincide.

*General Discussion.*

From an inspection of Fig. 7, in which several typical curves are collected, it appears that the higher melting-point curves (a) have a

greater initial fall, (b) are flatter in the neighbourhood of the minima, (c) have minima which occur higher up in the series.

If the initial fall in melting point is to be attributed to the greater association of the earlier members, as in the case of the fatty acids, it might be expected to become much less for a series of compounds like the tribromo-anilides, in which the diortho-grouping would prevent molecular association. This initial fall must then be due to some other cause. It should be noticed that it is at all events unconnected with the weight of the substituent radicle. Thus the anilides and *p*-toluidides have totally different types of curve, as likewise the *p*-bromo-anilides and the *o*-bromo-*p*-toluidides.

At a certain distance up the series, in most of the cases examined at about the fourteenth member, the curves tend to become parallel, rising somewhat less rapidly as the weight of the substituent group increases. It would seem then that at this stage the causes of the initial fall in melting point, and the variations in the early part of the curve generally, had been eliminated, and that some single factor, probably the molecular weight, was operative only.

The molecules of a solid may be regarded as being held together in a condition of strain by some force, possibly magnetic (Oxley), on the magnitude of which depend double refraction in particular and the physical properties of the solid generally. The energy of the molecules is almost entirely vibrational, half of which is kinetic and half potential. As the temperature rises the amplitude of vibration of the molecule increases, and when it becomes equal to the mean distance of the molecules apart, which is proportional to the cube root of the molecular volume, the substance melts (Lindemann). Equating the energy in terms of heat required to raise the molecule from the absolute zero to its melting point,  $T_s$ , with the vibrational energy of the molecule at this temperature, one obtains the expression

$$MsT_s = \kappa \cdot M \bar{V}^{1/3} \nu^2 \quad (\kappa = \text{const.}),$$

where  $M$  is the molecular weight,  $s$  the mean specific heat from the absolute zero to  $T_s$ ,  $\bar{V}$  the molecular volume, and  $\nu$  the characteristic vibration frequency of the molecule.

It is thus seen that the melting temperature is a function of the specific heat, the molecular volume, and the vibration frequency of the molecule. A suitable variation of these three values would be capable of causing the observed irregularities in the melting points of a series of compounds. This equation also shows that the magnitude of the melting point is independent of any association in the liquid phase, although it is probable that the factors causing

such association would effect the values of  $s$ ,  $l'$ , and  $v$  in the sense of increasing the value of  $T_s$ .

High up a series the density and specific heat of successive members become approximately constant, and then

$$T_s = \kappa' \cdot M^{1/2} \quad (\kappa' = \text{const.}).$$

Under such conditions  $v$  is probably some simple function of  $M$ , so that the melting point might be expected to depend on the magnitude of the molecular weight alone. Actually the empirical relation,

$$T_s = \kappa'' \cdot M^{1/3} \quad (\kappa'' = \text{const.}),$$

has been found, with two noticeable exceptions, to give a fair agreement, not only for the higher members of the substituted amides, but for other compounds also (table IV).

TABLE IV.

| Compound.  | Rise in m. p. for $2\text{CH}_2$ . |                  |
|--|------------------------------------|------------------|
|  | Experi-<br>mental. <sup>1</sup>    | From<br>formula. |
| $\text{C}_{14}$ anilide.....                                 | 5.0 <sup>2</sup>                   | 4.7 <sup>2</sup> |
| $\text{C}_{14}$ <i>p</i> -toluidide.....                     | 4.5                                | 4.6              |
| $\text{C}_{14}$ <i>o</i> -toluidide.....                     | 4.5                                | 4.6              |
| $\text{C}_{16}$ <i>p</i> -bromoanilide.....                  | 4.0                                | 4.0              |
| $\text{C}_{16}$ <i>o</i> -bromo- <i>p</i> -toluidide.....    | 4.0                                | 3.9              |
| $\text{C}_{16}$ $\alpha$ -bromo- $\beta$ -naphthylamide..... | 3.0                                | 3.2              |
| $\text{C}_{16}$ amide.....                                   | 3.0                                | 6.1              |
| $\text{C}_{16}$ $\beta$ -naphthylamide.....                  | 2.0                                | 4.3              |
| lacontane, $\text{C}_{30}\text{H}_{52}$ .....                | 3.9                                | 3.6              |
| lanthanone, $\text{C}_{13}\text{H}_{10}\text{O}$ .....       | 1.8                                | 2.2              |

<sup>1</sup> For the substituted amides, the mean difference between the  $\text{C}_{14}$  and  $\text{C}_{16}$  compounds was taken; in the other cases, a slight interpolation was necessary.

## EXPERIMENTAL.

The substituted amides obtained in this investigation were prepared in the following manner. About 1 gram of the fatty acid was mixed in a test-tube with slightly more than the theoretical quantity of thionyl chloride and heated to 100–120° in a sulphuric acid bath for about an hour. The theoretical quantity of base was then added, and the mixture further heated for half an hour to a somewhat higher temperature. The product was recrystallized from alcohol until the melting point was constant, and then finally from light petroleum, with which was mixed, in the case of the insoluble compounds, a small quantity of benzene.

The fatty acids employed were obtained from Kahlbaum. The purity of the solid acids was tested by determining their melting points; the liquid acids were either synthetic or were compared



with Merck's preparations by preparing a common derivative and testing by the method of mixed melting point. The bases were purified by several recrystallisations before being used for the preparations.

Repeated attempts were made to discover the existence of physical isomerides by recrystallising the same compound from different solvents and at different temperatures, and also by having present a trace of alkali or of acid in the solution. All these experiments, however, were without result.

All the melting-point determinations were made by the capillary tube method in a castor-oil bath with the same thermometer, which was compared from time to time with a standard one. When it happened that neighbouring members of a series melted at about the same temperature, their melting points were redetermined simultaneously.

The amides not containing bromine were analysed by the method of Dumas or Kjeldahl. The bromo-derivatives were analysed by the chromic acid method,\* which with practice enables an estimation to be made in about fifty minutes.

In table V are given the redetermined values of the melting points of the amides, anilides, and *p*-toluidides. The values given by other observers are included for the sake of comparison.

TABLE V.

| Compound.                    | Formula.         | M. p. | Previous observers.  |
|------------------------------|------------------|-------|--|
| <i>n</i> -Valeramide .....   | $C_5H_{11}ON$    | 106°  | 115° (Weidel); 105° (Fournier); 102° (Hofmann).                              |
| <i>n</i> -Hexoamide .....    | $C_6H_{13}ON$    | 101   | 100° (Hofmann).  |
| <i>n</i> -Heptoamide .....   | $C_7H_{15}ON$    | 96    | 96° (Hofmann); 95° (Mehlis); 93° (Fournier); 95° (Malherbe); 94° (Aschan).   |
| <i>n</i> -Octoamide .....    | $C_8H_{17}ON$    | 105   | 110° (Fellertar); 106° (Hofmann); 98° (Aschan).                              |
| <i>n</i> -Nonoamide .....    | $C_9H_{19}ON$    | 99    | 99° (Hofmann); 93° (Schalfejew).   |
| <i>n</i> -Decoamide .....    | $C_{10}H_{21}ON$ | 99    | 108° (Ehestadt); 98° (Hofmann).  |
| <i>n</i> -Undecoamide .....  | $C_{11}H_{23}ON$ | 99    | 103° (Ehestadt); 81° (Lwow).   |
| Lauramide .....              | $C_{12}H_{25}ON$ | 100   | 110° (Ehestadt); 102° (Krafft); 99° (Caspari); 97° (Lutz).                   |
| <i>n</i> -Tridecoamide ..... | $C_{13}H_{27}ON$ | 100   | 98° (Lutz).  |
| Myristamide .....            | $C_{14}H_{29}ON$ | 103   | 102° (Reimer).   |
| Palmitamide .....            | $C_{16}H_{33}ON$ | 106   | 107° (Krafft); 105° (Hell); 101° (Carlet).                                   |
| Stearamide .....             | $C_{18}H_{37}ON$ | 109   | 109° (Krafft); 108° (Hell); 107° (Carlet).                                   |
| <i>n</i> -Butyranilide ..... | $C_{10}H_{11}ON$ | 96    | 97° (Beneck); 93° (Fournier); 92° (Kelbe); 90° (Gerhardt); 90° (Autenrieth). |

\* Robertson, T., 1915, 107, 902. The following slight modifications have been introduced. Sodium peroxide is used instead of perhydrol, and *N*/20-silver nitrate and thiocyanate in place of *N*/10-solutions.

## SUBSTITUTED AMIDES OF THE NORMAL FATTY ACIDS. 1221

TABLE V (continued).

| Compound.                             | Formula.                           | M. p. | Previous observers.                              |
|---------------------------------------|------------------------------------|-------|--|
| <i>n</i> -Valeranilide .....          | C <sub>11</sub> H <sub>19</sub> ON | 63°   | 63° (Fournier); 61° (Easterfield); 60° (Majima). |
| <i>n</i> -Hexoanilide .....           | C <sub>12</sub> H <sub>17</sub> ON | 92    | 95° (Kelbe).                                     |
| <i>n</i> -Heptoanilide .....          | C <sub>13</sub> H <sub>19</sub> ON | 65    | 71° (Lwow).                                      |
| <i>n</i> -Octoanilide .....           | C <sub>14</sub> H <sub>21</sub> ON | 55    | 57° (Robertson).                                 |
| <i>n</i> -Nonoanilide .....           | C <sub>15</sub> H <sub>23</sub> ON | 57    | 57° (Robertson).                                 |
| <i>n</i> -Decoanilide .....           | C <sub>16</sub> H <sub>25</sub> ON | 70    | 61° (Robertson).                                 |
| <i>n</i> -Undecoanilide .....         | C <sub>17</sub> H <sub>27</sub> ON | 71    | 68° (Bagard); 64° (Robertson).                   |
| Lauranilide .....                     | C <sub>18</sub> H <sub>29</sub> ON | 78    | 76° (Caspari); 68° (Robertson).                  |
| <i>n</i> -Butyro- <i>p</i> -toluidide | C <sub>11</sub> H <sub>17</sub> ON | 75    | 74° (Robertson).                                 |
| <i>n</i> -Valero- " "                 | C <sub>12</sub> H <sub>19</sub> ON | 74    | 72° (Robertson).                                 |
| <i>n</i> -Hexo- " "                   | C <sub>13</sub> H <sub>21</sub> ON | 73    | 75° (Robertson).                                 |
| <i>n</i> -Hepto- " "                  | C <sub>14</sub> H <sub>23</sub> ON | 81    | 80° (Robertson); 79° (Kipping).                  |
| <i>n</i> -Octo- " "                   | C <sub>15</sub> H <sub>25</sub> ON | 70    | 67° (Robertson).                                 |
| <i>n</i> -Nono- " "                   | C <sub>16</sub> H <sub>27</sub> ON | 84    | 81° (Robertson).                                 |
| <i>n</i> -Deco- " "                   | C <sub>17</sub> H <sub>29</sub> ON | 78    | 80° (Robertson).                                 |
| <i>n</i> -Undeco- " "                 | C <sub>18</sub> H <sub>31</sub> ON | 80    | 75° (Bagard); 73° (Robertson).                   |
| Lauro- " "                            | C <sub>19</sub> H <sub>33</sub> ON | 87    | 81° (Robertson).                                 |
| Myristo- " "                          | C <sub>21</sub> H <sub>37</sub> ON | 93    | 93° (Robertson).                                 |
| Palmito- " "                          | C <sub>23</sub> H <sub>39</sub> ON | 98    | 96° (Robertson).                                 |
| Stearo- " "                           | C <sub>27</sub> H <sub>41</sub> ON | 102   | 98° (Robertson).                                 |

In table VI are given the new compounds prepared in this investigation, with melting points and analytical results; the percentage values refer to bromine in the case of the bromo-derivatives and to nitrogen for the other compounds.

TABLE VI.

| Compound.                                      | Formula.                           | M. p. | Found per cent. | Calc. per cent. |
|--|------------------------------------|-------|-----------------|-----------------|
| <i>n</i> -Tridecoanilide .....                 | C <sub>14</sub> H <sub>31</sub> ON | 80°   | N 4.7           | 4.8             |
| <i>n</i> -Trideco- <i>p</i> -toluidide .....   | C <sub>26</sub> H <sub>33</sub> ON | 88    | 4.4             | 4.6             |
| <i>n</i> -Butyro- <i>p</i> -toluidide .....    | C <sub>11</sub> H <sub>19</sub> ON | 79    | 8.0             | 7.8             |
| <i>n</i> -Hexo- " "                            | C <sub>12</sub> H <sub>17</sub> ON | 71    | 6.6             | 6.8             |
| <i>n</i> -Hepto- " "                           | C <sub>13</sub> H <sub>19</sub> ON | 68    | 6.5             | 6.4             |
| <i>n</i> -Octo- " "                            | C <sub>14</sub> H <sub>21</sub> ON | 69    | 6.2             | 6.0             |
| <i>n</i> -Nono- " "                            | C <sub>15</sub> H <sub>23</sub> ON | 73    | 5.4             | 5.7             |
| <i>n</i> -Deco- " "                            | C <sub>16</sub> H <sub>25</sub> ON | 76    | 5.2             | 5.3             |
| <i>n</i> -Undeco- " "                          | C <sub>17</sub> H <sub>27</sub> ON | 78    | 5.0             | 5.0             |
| Lauro- " "                                     | C <sub>19</sub> H <sub>31</sub> ON | 83    | 4.9             | 4.8             |
| <i>n</i> -Trideco- " "                         | C <sub>21</sub> H <sub>33</sub> ON | 85    | 4.8             | 4.6             |
| Myristo- " "                                   | C <sub>23</sub> H <sub>35</sub> ON | 88    | 4.5             | 4.4             |
| Stearo- " "                                    | C <sub>27</sub> H <sub>41</sub> ON | 97    | 3.8             | 3.8             |
| <i>n</i> -Butyro- $\beta$ -naphthylamide ..... | C <sub>21</sub> H <sub>23</sub> ON | 125   | 6.8             | 6.6             |
| <i>n</i> -Valero- " "                          | C <sub>22</sub> H <sub>25</sub> ON | 112   | 6.2             | 6.2             |
| <i>n</i> -Hexo- " "                            | C <sub>23</sub> H <sub>27</sub> ON | 107   | 5.6             | 5.8             |
| <i>n</i> -Hepto- " "                           | C <sub>24</sub> H <sub>29</sub> ON | 101   | 5.7             | 5.6             |
| <i>n</i> -Octo- " "                            | C <sub>25</sub> H <sub>31</sub> ON | 103   | 5.3             | 5.2             |
| <i>n</i> -Nono- " "                            | C <sub>26</sub> H <sub>33</sub> ON | 103   | 5.1             | 4.9             |
| <i>n</i> -Deco- " "                            | C <sub>27</sub> H <sub>35</sub> ON | 104   | 4.8             | 4.7             |
| Lauro- " "                                     | C <sub>29</sub> H <sub>37</sub> ON | 106   | 4.4             | 4.4             |
| <i>n</i> -Trideco- " "                         | C <sub>31</sub> H <sub>39</sub> ON | 107   | 4.1             | 4.2             |
| Myristo- " "                                   | C <sub>33</sub> H <sub>41</sub> ON | 108   | 4.1             | 4.0             |
| Stearo- " "                                    | C <sub>37</sub> H <sub>45</sub> ON | 112   | 3.3             | 3.4             |

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TABLE VI (continued).

| Compound.  | Formula.  | M. p. | Found<br>per<br>cent. | Calc.<br>per<br>cent. |
|--|---|-------|-----------------------|-----------------------|
| <i>n</i> -Butyro- <i>p</i> -bromoanilide.....      | C <sub>10</sub> H <sub>13</sub> ONBr              | 115°  | Br=33.4               | 33.1                  |
| <i>n</i> -Valero-      "      .....                | C <sub>11</sub> H <sub>14</sub> ONBr              | 108   | 31.3                  | 31.3                  |
| <i>n</i> -Hexo-      "      .....                  | C <sub>12</sub> H <sub>15</sub> ONBr              | 105   | 30.0                  | 29.6                  |
| <i>n</i> -Hepto-      "      .....                 | C <sub>13</sub> H <sub>16</sub> ONBr              | 98    | 28.0                  | 28.1                  |
| <i>n</i> -Octo-      "      .....                  | C <sub>14</sub> H <sub>17</sub> ONBr              | 103   | 26.8                  | 26.9                  |
| <i>n</i> -Nono-      "      .....                  | C <sub>15</sub> H <sub>18</sub> ONBr              | 100   | 26.0                  | 25.7                  |
| <i>n</i> -Deco-      "      .....                  | C <sub>16</sub> H <sub>19</sub> ONBr              | 102   | 24.6                  | 24.6                  |
| <i>n</i> -Undeco-      "      .....                | C <sub>17</sub> H <sub>20</sub> ONBr              | 102   | 23.7                  | 23.7                  |
| Lauro-      "      .....                           | C <sub>18</sub> H <sub>21</sub> ONBr              | 104   | 22.3                  | 22.8                  |
| Myristo-      "      .....                         | C <sub>20</sub> H <sub>23</sub> ONBr              | 107   | 20.8                  | 20.9                  |
| Palmito-      "      .....                         | C <sub>22</sub> H <sub>25</sub> ONBr              | 110   | 19.8                  | 19.5                  |
| Stearo-      "      .....                          | C <sub>24</sub> H <sub>27</sub> ONBr              | 114   | 18.4                  | 18.3                  |
| Propio- <i>o</i> -bromo- <i>p</i> -toluidide ..... | C <sub>10</sub> H <sub>13</sub> ONBr              | 111   | 33.4                  | 33.1                  |
| <i>n</i> -Butyro-      "      .....                | C <sub>11</sub> H <sub>14</sub> ONBr              | 90    | 30.9                  | 31.3                  |
| <i>n</i> -Valero-      "      .....                | C <sub>12</sub> H <sub>15</sub> ONBr              | 100   | 29.5                  | 29.6                  |
| <i>n</i> -Hexo-      "      .....                  | C <sub>13</sub> H <sub>16</sub> ONBr              | 84    | 28.5                  | 28.1                  |
| <i>n</i> -Hepto-      "      .....                 | C <sub>14</sub> H <sub>17</sub> ONBr              | 90    | 26.8                  | 26.9                  |
| <i>n</i> -Octo-      "      .....                  | C <sub>15</sub> H <sub>18</sub> ONBr              | 78    | 25.5                  | 25.7                  |
| <i>n</i> -Nono-      "      .....                  | C <sub>16</sub> H <sub>19</sub> ONBr              | 86    | 24.7                  | 24.6                  |
| <i>n</i> -Deco-      "      .....                  | C <sub>17</sub> H <sub>20</sub> ONBr              | 82    | 23.7                  | 23.7                  |
| <i>n</i> -Undeco-      "      .....                | C <sub>18</sub> H <sub>21</sub> ONBr              | 91    | 22.3                  | 22.6                  |
| Lauro-      "      .....                           | C <sub>19</sub> H <sub>22</sub> ONBr              | 85    | 21.3                  | 21.7                  |
| <i>n</i> -Trideco-      "      .....               | C <sub>20</sub> H <sub>23</sub> ONBr              | 95    | 21.0                  | 20.9                  |
| Myristo-      "      .....                         | C <sub>22</sub> H <sub>25</sub> ONBr              | 89    | 20.6                  | 20.3                  |
| Stearo-      "      .....                          | C <sub>24</sub> H <sub>27</sub> ONBr              | 97    | 17.7                  | 17.7                  |
| Propio- <i>o</i> -bromo- $\beta$ -naphthylamide    | C <sub>22</sub> H <sub>17</sub> ONBr              | 139   | 29.0                  | 28.8                  |
| <i>n</i> -Butyro-      "      .....                | C <sub>23</sub> H <sub>18</sub> ONBr              | 139   | 27.3                  | 27.4                  |
| <i>n</i> -Valero-      "      .....                | C <sub>24</sub> H <sub>19</sub> ONBr              | 136   | 25.9                  | 26.2                  |
| <i>n</i> -Hexo-      "      .....                  | C <sub>25</sub> H <sub>20</sub> ONBr              | 120   | 25.4                  | 25.1                  |
| <i>n</i> -Hepto-      "      .....                 | C <sub>26</sub> H <sub>21</sub> ONBr              | 111   | 23.9                  | 24.0                  |
| <i>n</i> -Octo-      "      .....                  | C <sub>27</sub> H <sub>22</sub> ONBr              | 104   | 23.4                  | 23.1                  |
| <i>n</i> -Nono-      "      .....                  | C <sub>28</sub> H <sub>23</sub> ONBr              | 103   | 22.1                  | 22.1                  |
| <i>n</i> -Deco-      "      .....                  | C <sub>29</sub> H <sub>24</sub> ONBr              | 102   | 21.7                  | 21.3                  |
| Lauro-      "      .....                           | C <sub>30</sub> H <sub>25</sub> ONBr              | 99    | 19.5                  | 19.8                  |
| Myristo-      "      .....                         | C <sub>32</sub> H <sub>27</sub> ONBr              | 100   | 18.6                  | 18.5                  |
| Stearo-      "      .....                          | C <sub>34</sub> H <sub>29</sub> ONBr              | 106   | 16.4                  | 16.4                  |
| <i>n</i> -Butyro-2:4:6-tribromoanilide             | C <sub>10</sub> H <sub>10</sub> ONBr <sub>3</sub> | 179   | 58.6                  | 58.3                  |
| <i>n</i> -Hexo-      "      .....                  | C <sub>12</sub> H <sub>11</sub> ONBr <sub>3</sub> | 136   | 56.3                  | 56.2                  |
| <i>n</i> -Hepto-      "      .....                 | C <sub>13</sub> H <sub>12</sub> ONBr <sub>3</sub> | 134   | 54.9                  | 54.4                  |
| <i>n</i> -Octo-      "      .....                  | C <sub>14</sub> H <sub>13</sub> ONBr <sub>3</sub> | 131   | 52.8                  | 52.6                  |
| <i>n</i> -Nono-      "      .....                  | C <sub>15</sub> H <sub>14</sub> ONBr <sub>3</sub> | 131   | 51.3                  | 51.2                  |
| <i>n</i> -Deco-      "      .....                  | C <sub>16</sub> H <sub>15</sub> ONBr <sub>3</sub> | 129   | 49.9                  | 49.7                  |
| <i>n</i> -Undeco-      "      .....                | C <sub>17</sub> H <sub>16</sub> ONBr <sub>3</sub> | 129   | 48.0                  | 48.2                  |
| Lauro-      "      .....                           | C <sub>18</sub> H <sub>17</sub> ONBr <sub>3</sub> | 126   | 46.8                  | 46.9                  |
| Myristo-      "      .....                         | C <sub>20</sub> H <sub>19</sub> ONBr <sub>3</sub> | 124   | 44.0                  | 44.5                  |
| Palmitic      "      .....                         | C <sub>22</sub> H <sub>21</sub> ONBr <sub>3</sub> | 124   | 42.1                  | 42.3                  |
| Stearo-      "      .....                          | C <sub>24</sub> H <sub>23</sub> ONBr <sub>3</sub> | 126   | 40.6                  | 40.3                  |

The problem of investigating the relationship between melting point and chemical composition is being extended in other directions to the substituted amides of dibasic and  $\alpha$ -substituted acids. The mathematical interpretation suggested above is from the nature

of things only fragmentary and imperfect, and it has not been possible to suggest a reason why compounds containing the grouping  $\text{CO}\cdot\text{NH}\cdot$  or  $\text{CO}\cdot\text{O}\cdot$  should form series so different in character from other series. The Quantum Theory has not yet been extended to include the investigation of complex molecules, but there is no doubt that a knowledge of the vibration frequency ( $\nu$ ), and the specific heat over a wide range of temperature, is essential for a complete mathematical treatment. The determination of the melting points of a large group of similar compounds is at all events a step in this direction.

My thanks are due to Dr. P. A. Levene for a specimen of trioleic acid, and to the Chemical Society for a grant, which has partly defrayed the cost of the investigation.

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## Organic Chemistry.

**Manufacture of Amyl Acetate and its Homologues from Chloro-hydrocarbons of the Paraffin Series.** G. G. OBERPÉLL and H. T. BOYD (U.S. Pat. 1302583; from *J. Soc. Chem. Ind.*, 1919, **38**, 554A).—Chloro-paraffins are converted into acetic esters by treatment with an alkali acetate and acetic acid in presence of an alkali sulphate. G. F. M.

**The Insecticidal Principle of Chrysanthemum cinerariifolium (Insect Powder).** RYŌ YAMAMOTO (*Ber. Ōhara Inst. landw. Forsch.*, 1918, **1**, 389—398).—A yellow, viscous oil having powerful insecticidal properties was isolated from the powdered flowers of *Chrysanthemum cinerariifolium*, the yield being 0.8%. The oil had a saponification number of 216 and an iodine number of 116; from the saponified substance, two alcohols having the formulæ  $C_{21}H_{34}O$ , m. p.  $199^{\circ}$ , and  $C_{27}H_{46}O$ , m. p.  $175-179^{\circ}$ , and two fatty acids having the formulæ  $C_{10}H_{18}O_2$  and  $C_{16}H_{32}O_2$  (palmitic), were separated. The insecticidal power of the oil was reduced when the oil was heated at  $100^{\circ}$  or exposed to air for a long period. W. P. S.

**Action of Methyl Sulphate and Methyl Alkali Sulphate on Dry Alkali Chlorides and Bromides.** J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, **169**, 435—437).—When methyl sulphate is heated with sodium chloride, reaction at first appears to take place according to the equation  $Me_2SO_4 + NaCl = NaMeSO_4 + MeCl$ , and is followed by a reaction shown by the equation  $2NaMeSO_4 = Na_2S_2O_7 + OMe_2$ . The residue, however, always contains normal sodium sulphate, and the quantities of the two gases formed are not theoretical; methyl chloride is in excess. If equimolecular quantities of methyl sulphate and potassium chloride are heated together, two-thirds of the methyl sulphate reacts according to the second of the above equations, the remainder reacting with the potassium chloride,  $KMeSO_4 + KCl = K_2SO_4 + MeCl$ . If two molecules of potassium chloride are used, the latter reaction disappears almost completely, and the reaction is represented by the equation  $2Me_2SO_4 + 2KCl = 2MeCl + OMe_2 + K_2S_2O_7$ . Bromides behave in a similar way to chlorides in the reactions. W. P. S.

**Interaction between Methyl Sulphate and Chloro-sulphonic Acid.** CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1919, **169**, 338—341).—Equimolecular proportions of methyl sulphate and chlorosulphonic acid slowly react according to the equation  $SO_2(OMe)_2 + SO_2Cl \cdot OH = SO_2Cl \cdot OMe + SO_2(OH) \cdot OMe$ ,

an equilibrium being reached at the end of a month, when the reaction has proceeded to the extent of 36% to the right. If kept for a further period, a change in acidity slowly occurs, owing to the formation of sulphuric acid, according to the equation  $\text{SO}_3(\text{OH})\cdot\text{OMe} + \text{SO}_2\text{Cl}\cdot\text{OH} \rightleftharpoons \text{SO}_2\text{Cl}\cdot\text{OMe} + \text{H}_2\text{SO}_4$ ; this change at the end of 138 days has not quite reached equilibrium. When, on the other hand, the reaction mixture is subjected to vacuum distillation, the two initial materials practically disappear, and a yield of 50% of methyl chlorosulphonate is obtained, together with small quantities of hydrogen chloride, methyl chloride, and a residue of sulphuric acid.

G. F. M.

**Wax of a South Brazilian Wild Bee.** J. GADAMER (*Arch. Pharm.*, 1917, 255, 425—441).—The characters and composition of wax produced by a wild bee, probably of the species *Melipona* or *Trigona*, are described. [See *J. Soc. Chem. Ind.*, 1919, 730A.]

T. H. P.

**Lipoids of the Heart Muscle.** P. A. LEVENE and S. KOMATSU (*J. Biol. Chem.*, 1919, 39, 83—89).—The analysis of the so-called lecithin fraction obtained from heart muscle demonstrates that this fraction is a mixture of lecithin and kephalin. When reduced by means of hydrogen in the presence of colloidal palladium, a product was obtained having all the properties of the crude hydrolecithin obtained from egg-yolk (Levene and West, A., 1918, i, 288, 421). From this mixture, by fractionation, hydrolecithin and hydrokephalin were isolated.

The opinion expressed by Fränkel and Linnert (A., 1910, i, 295) that individual organs of the same animal contain specific phosphatides appears to lack support. There is rather an indication that the number of individual lipoids is limited, and that practically all animal organs contain the same lipoids.

J. C. D.

**Kephalin. VI. The Bearing of Cuorin on the Structure of Kephalin.** P. A. LEVENE and S. KOMATSU (*J. Biol. Chem.*, 1919, 39, 91—104).—The components of kephalin hitherto isolated are phosphoric acid, glycerol, aminoethyl alcohol, and stearic and linoleic acids. A molecule composed of equimolecular proportions of these would demand a different percentage composition from that usually found. The discrepancy could be explained on one of three grounds: first, that kephalin possesses a structure different from the one expressed by the above method; secondly, that kephalin isolated by the usual methods represented a substance modified in the course of preparation; and thirdly, that a substance of unknown composition was present as an impurity. The recent work of Levene and West (A., 1918, i, 421) on the preparation of a reduced kephalin possessing an elementary composition required by a molecule constituted as above excludes the first of the three alternatives. The work recorded in this paper shows that kephalin as usually prepared is a mixture of true kephalin with its own decomposition products. This explains the widely different

analytical data recorded by previous workers. One of the decomposition products is kephalin from which one fatty acid has been removed either by chemical manipulation or by enzymes. Substances were also obtained which consisted of products of deeper deterioration than the loss of one acid molecule. This conclusion was arrived at in the course of an investigation into the chemical nature of cuorin.

Support is given to the view of Maclean ("The Lipins," London, 1918, 52), who doubted that cuorin is an individual substance. The greater part of cuorin is made up of crude kephalin.

J. C. D.

**Preparation of Monochloroacetic Acid.** L. J. SIMON and G. CHAVANNE (U.S. Pat. 1304108; from *J. Soc. Chem. Ind.*, 1919, 38, 553A).—Monochloroacetic acid is prepared by heating trichloroethylene with sulphuric acid containing a small amount of water.

G. F. M.

**Oxidation of Lactic Acid by Bacteria with Formation of Pyruvic Acid and Ketonic Substances.** P. MAZÉ (*Compt. rend. Soc. biol.*, 1918, 81, 1150—1152; from *Chem. Zentr.*, 1919, i, 960).—The author has isolated a dozen types of bacteria which have the power of forming pyruvic acid and ketonic substances by the oxidation of lactic acid in a purely mineral nutrient solution and with calcium lactate as the sole source of carbon. The same types also produce pyruvic acid from similar solutions containing sugar, from which they form lactic acid; only in one instance does the alcoholic fermentation of sugar also occur. The course of the action has been more closely studied with six varieties, the pyruvic acid being estimated colorimetrically by Simon's reaction; for this purpose, the content of the solution must lie between 0.1 and 1%. Formation and decomposition of pyruvic acid occur at different rates with the various species. The yield of acetic acid varies from traces to more than 50% of the lactic acid decomposed, but formic acid is never produced. Two species produce, further, acetylmethylcarbinol and dimethyl diketone, whilst one species produces the latter only. The processes involved are indicated by the equations  $\text{CH}_3\text{CH}(\text{OH})\cdot\text{CO}_2\text{H} + \text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{O} = \text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{COMe} + 2\text{CO}_2 + \text{H}_2\text{O}$  and  $2\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{O} = \text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_3 + 2\text{CO}_2 + \text{H}_2\text{O}$ . Dimethyl diketone might possibly be formed by direct oxidation of the secondary alcoholic group of acetylmethylcarbinol, but the complete absence of butylene glycol renders this improbable.

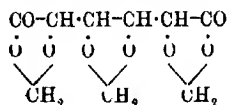
H. W.

**Quantitative Studies on the Succinic Oxidone of Battelli and Stern.** HANS EINBECK (*Biochem. Zeitsch.*, 1919, 95, 296—305. Compare Battelli and Stern, *A.*, 1913, i, 929).—It appears probable that two quite distinct processes may take place when succinic acid is acted on by muscle pulp in the presence of oxygen. First, there is the elimination of two atoms of hydrogen with the formation of fumaric acid. This reaction is quantitative,



the amount of oxygen required being proportional to the amount of succinic acid in the reaction mixture. Then there is the addition of a molecule of water at the unsaturated linking of the fumaric acid, with the formation of *i*-malic acid. This reaction is not quantitative, but tends to an equilibrium, at which approximately a quarter of the fumaric acid remains unchanged. J. C. D.

**Behaviour of the Methylene Group United to the Carboxyl Group in Trimethylenesaccharic Acid.** CRESARE PADERI (*Arch. farm. sper. sci. aff.*, 1918, 26, 274—282; from *Chem. Zentr.*, 1919, iii, 65).—Opportunity is afforded by trimethylenesaccharic acid (annexed formula) of further investigation



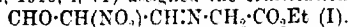
of the author's views on the relative stability of methyl groups which esterify hydroxy-groups or hydroxy- and carboxyl groups respectively (compare A., 1917, i, 716). The acid is hydrolysed by boiling water containing a small quantity of sulphuric acid to monomethylenesaccharic acid and formaldehyde. A similar fission appears to occur in the rabbit, since formaldehyde can be detected in the urine after administration of the acid. H. W.

**Linoleic Acid and its Derivatives.** KATSUMI TAKAMASHI (*J. Tokyo Chem. Soc.*, 1919, 40, 233—239).—Linoleic acid can be estimated only by converting it into its derivatives. Physical and chemical properties, however, of both the bromo- and hydroxy-derivatives into which linoleic acid is ordinarily converted are confusing according to the different authors (compare Reformatzky, A., 1890, 362). Furthermore, the value obtained by the tetrabromostearic acid method is invariably less than that calculated from the iodine number in the presence of another unsaturated fatty acid. In order to investigate the source of this discrepancy, the author made extensive studies of the properties of various derivatives of linoleic acid. Linoleic acid is first separated by brominating linoleic acid from oil of rice bran and soja bean. This tetrabromostearic acid, which he designates as (A)-bromo-derivative, after repeated crystallisation from light petroleum, forms white, needle-shaped crystals, m. p. 114°. It is soluble in ether, but insoluble in light petroleum at the ordinary temperature. When converted into the methyl ester by Rollett's method, and hydrolysed to linoleic acid, a 90% yield calculated on the basis of the (A)-bromo-derivative, or 97% if calculated on the basis of its methyl ester, was obtained. An analysis shows its composition to be exactly that of linoleic acid. When this is again brominated, it yields three types of bromo-derivatives, regardless of the kinds of solvent used: (α) m. p. 113.5—114°, containing 53.38% of Br, insoluble in light petroleum; (β) m. p. 59—60°, containing 53.35% of Br, soluble in light petroleum; (γ) liquid, containing 52.86% of Br, soluble in light petroleum. Since the theoretical value for

tetrabromostearic acid,  $C_{18}H_{32}O_2Br_4$ , is 53.33% of Br, he concludes all these three varieties of bromo-derivatives must be tetrabromostearic acid. The yields of the three derivatives vary somewhat with the types of solvent used. With light petroleum as solvent, 43—46% of the total yield is in the  $\alpha$ -form, the remaining 49.2% to 52.66% being  $\beta$  and  $\gamma$ ; with carbon tetrachloride, 39%  $\alpha$  and 56%  $\beta$  and  $\gamma$ ; with ethyl ether, 47%  $\alpha$ , 51.77% of  $\beta$  and  $\gamma$ ; with glacial acetic acid, 35% of  $\alpha$ . In all cases, the  $\alpha$ -form, which possesses exactly the same physical properties as the parent compound (that is, tetrabromostearic acid, m. p. 114°, soluble in light petroleum), is obtained only in a quantity of 49% of the (A)-bromo-derivative, the remaining portion being the same tetrabromostearic acid but having entirely different physical properties. When the  $\alpha$ -variety is again reduced to linoleic acid and brominated for a third time, it gives 42.4—46% of the  $\alpha$ -form and 52.8—55.8% of  $\beta$  and  $\gamma$ . From the  $\beta$ -form, 36.7% of the  $\alpha$ , 48% of  $\beta$ , and 22.4% of  $\gamma$ ; from the  $\gamma$ -form, 24—26% of  $\alpha$ , 8.05—8.4% of  $\beta$ , but 67.95—65.35% of  $\gamma$  are obtained. In general, all three racemic varieties of tetrabromostearic acid can be reduced to linoleic acid, and on further bromination each yields three varieties of bromo-derivatives, always, however, giving most of its own kind. The oxidation products of linoleic acid obtained from the  $\alpha$ - and  $\beta$ -forms are a large quantity of sativic acid, m. p. 174°, and a small quantity of another tetrahydroxystearic acid, m. p. 135°. The linoleic acid obtained from the  $\gamma$ -form yields neither sativic acid nor the other tetrahydroxystearic acid, but gives an acid,  $C_{16}H_{31}O_3 \cdot OH$ , soluble in water and a rosin-like substance insoluble in water and having the formula  $(C_8H_{15}O)_2$ . By applying the same method to the natural linoleic acid in the presence of unsaturated fatty acids, only 40% of the original amount of linoleic acid is obtained as the crystallised tetrabromostearic acid insoluble in light petroleum. The author proposes, therefore, a factor 2.5 to be used for linoleic acid estimations: it is to be isolated as the insoluble tetrabromostearic acid. Several analytical data are given to show that this factor is most satisfactory.

CHEMICAL ABSTRACTS.

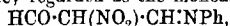
**Condensation of Amino-compounds with Nitromalon-aldehyde.** WILLIAM J. HALE and EDWARD M. HONAN (*J. Amer. Chem. Soc.*, 1919, **41**, 770—776).—To the aldehydic intermediate product formed in the preparation of carbopyrrolic esters by the condensation of aminoacetic esters with nitromalon-aldehyde, Hale and Hoyt (A., 1916, i, 71) assigned the constitution



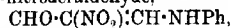
It is now found that such intermediate product is capable of formation in dilute alkaline solution, from which it separates readily. The substance separating is not, however, a salt, and is transformed by warm alkali into a pyrrole derivative, which the Hinsberg reaction and the Liebermann nitrosoamine reaction show to be a secondary amine. This intermediate compound must therefore have the constitution  $CHO \cdot C(NO_2) \cdot CH \cdot NH \cdot CH_2 \cdot CO_2Et$ , the

isonitro-compound (I) first produced undergoing intramolecular rearrangement with transfer of the labile hydrogen atom from the central carbon to the nitrogen.

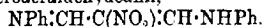
The assumption that the intermediate compound possessed the structure (I) was based on the results of Hill and Torrey (A., 1899, i, 788), who ascribed similar constitutions to a number of products resulting from the condensation of nitromalonaldehyde with amino-derivatives. With aniline, these authors obtained two compounds which they regarded as the monoanil,



and the dianil,  $\text{NPh}\cdot\text{CH}\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}\cdot\text{NPh}$ ; neither of these compounds exhibits any tendency to form salts, and as they are now found to be secondary amines, they must be regarded respectively as  $\beta$ -anilino- $\alpha$ -nitroacetaldehyde,

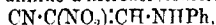


and  $\beta$ -anilino- $\alpha$ -nitroacetaldehydeanil,



The similar compounds furnished by *p*-toluidine and by methylamine and its derivatives must receive analogous formulæ.

The action of 1 mol. of hydroxylamine on nitromalonaldehyde gives an unstable compound which immediately undergoes intramolecular condensation to a  $\beta$ -nitroisoxazole, whereas excess of hydroxylamine gives a dioxime stable in alkaline solution. The action of aniline hydrochloride on the sodium salt of this dioxime precipitates Hill and Hale's anil-oxime (A., 1903, i, 401), which is formed also by the interaction of hydroxylamine and the so-called monoanil (see above), and must therefore be a  $\beta$ -anilino- $\alpha$ -nitroacetaldoxime,  $\text{NOH}\cdot\text{CH}\cdot\text{C}(\text{NO}_2)\cdot\text{CH}\cdot\text{NHPh}$ ; dehydration of this oxime gives a  $\beta$ -anilino- $\alpha$ -nitroacrylonitrile,



which Hill and Hale termed a nitrile-anil.

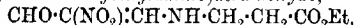
These facts render necessary a modification of Hale and Hoyt's interpretation (*loc. cit.*) of the condensation of nitromalonaldehyde with glycine ester; no rearrangement in the pyrrole molecule is necessary for condensation after the intramolecular rearrangement of compound (I).

The condensation of nitromalonaldehyde with  $\beta$ -alanine ethyl ester proceeds easily in slightly alkaline solution or in presence of sodium acetate.  $\beta$ -( $\beta$ -carbethoxyethylamino)- $\alpha$ -nitroacetaldehyde being formed. Further intramolecular condensation sufficient to render possible the isolation of a pyrrole could not be effected, the only indication of the formation of a pyrrole derivative being the reddening of a pine splinter held in the vapour produced when the compound was heated with concentrated hydrochloric acid.

The results obtained lead to the conclusion that, in aliphatic imino-compounds presenting an aldehyde group in such position that its possible inter-reaction with a methylene group adjacent to the imino-group may lead to a pyrrole, this condensation is highly favoured when the methylene group is attached to a carbethoxyl or other negative component. If, however, the carbethoxyl group

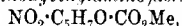
is once removed from the particular methylene group by the interposition of another methylene group, the influence of the carbethoxyl group becomes so slight that neither the first nor the second methylene group exhibits any marked tendency to condense with the aldehyde group.

*α-Nitro-β-(β-carbomethoxyethylamino)acraldehyde,*



forms colourless prisms, m. p. 79°, and gives various reactions for aldehydes and also Liebermann's nitrosoamine reaction.

*α-Nitro-β-(β-carbomethoxyethylamino)acraldehyde,*



forms colourless leaflets, m. p. 66°, and gives the same reactions as the preceding compound.

T. H. P.

### Thiocyanoacetone and its Derivatives and Isomerides.

JOSEPH TCHERNIAC (T., 1919, 115, 1071—1090).

**Photosynthesis of Formaldehyde and Sugar.** P. R. KÖGEL (*Biochem. Zeitsch.*, 1919, 95, 313—316).—A theoretical consideration, in which changes of the keto-enol type are held to be of importance in the photosynthesis of formaldehyde and sugar.

J. C. D.

**Degradation of Sugars by Enzymes.** H. VON EULER and O. SVANBERG (*Zeitsch. physiol. Chem.*, 1919, 105, 187—239).—The course of the fermentation of sugars by a top yeast and a torula in an alkaline medium ( $p_{\text{H}}=8$ ) has been studied. Under these conditions, alcohol and carbon dioxide are produced in equivalent amounts representing, for both products, 30—33% of the fermented sugar. Dextrose and levulose, as well as invert-sugar, are rapidly fermented at  $p_{\text{H}}=8$ , but mannose and galactose are less readily attacked. Sucrose is fermented as rapidly as dextrose at this degree of alkalinity, but maltose remains untouched. These observations indicate that invertase is active at  $p_{\text{H}}=8$ , but that maltase is not. The inversion of sucrose was quantitatively studied as far as  $p_{\text{H}}=8.5$  by repressing the fermentation by means of additions of toluene. The influence of a number of poisons on the fermentation in an alkaline medium is described. More or less marked inhibition was caused by chloroform, toluene, acetaldehyde, aniline, pyridine, resorcinol, sodium picrate, and phenol. Sodium salicylate caused a slightly increased rate of fermentation, whilst sodium lactate, chloroacetic acid, adrenaline, thyroid extract, and sodium thiosulphate had no appreciable effect. Drying at the ordinary temperature did not affect the activity of a yeast at  $p_{\text{H}}=8$ . The growth of yeasts in alkaline solutions has also been investigated.

J. C. D.

**Occurrence of Difficultly Reducing Carbohydrates in Urine.** RAGNAR BERG (*Deut. Med. Woch.*, 1919, 45, 435—436; from *Chem. Zentr.*, 1919, iii, 33).—It has long been known that certain urines which do not contain dextrose have the

power of reducing copper sulphate; the solution becomes milky, and finally, particularly when preserved, a yellow, more or less heavy, flocculent precipitate separates which differs completely from the heavy, red precipitate produced by sugar. The author has been able to isolate the difficultly reducing sugar, which appears to be identical with Leo's sugar, in the form of colourless needles, about 2 mm. in length. It is found that urine (in the presence or absence of sugar), which gives the characteristic reaction after fermentation, also exhibits levorotation. The reaction is frequently observed in cases of diabetes and neurasthenia, and particularly of gout. The author therefore designates the substance *arthritisose*.  
H. W.

**Chitose.** WALTHER ARMBRECHT (*Biochem. Zeitsch.*, 1919, 95, 108—123).—Chitosan is completely dissolved by the action of nitrous acid. The solution contains carbohydrates of more than one type, but no crystalline sugar could be isolated. A crystalline osazone, m. p. 202°, was isolated from this mixture. This product is apparently identical with the osazone of chitose. From the products obtained by oxidising the crude "chitose syrup" with nitric acid, a monocarboxylic acid was obtained, which forms a cinchonine salt, colourless prisms, m. p. 200°, and may possibly contain a hydrofuran ring.  
J. C. D.

**Epifucose.** E. VOTOČEK and J. ČERVÝ (*Zeitsch. Zuckerind. Böhm.*, 1917, 42, 215—217).—Fuconic acid is converted into epifuconic acid by treatment with pyridine and water, and the lactone of the latter acid is reduced by sodium amalgam to *epifucose*, which was isolated as a sweet, viscous, pale yellow syrup, and did not crystallise even after preservation during six months; it has  $[\alpha]_D^{20}$  ca -9°. The phenylosazone, m. p. 177—178° (decomp.), and the *p*-bromophenylosazone, m. p. 204°, are identical with the products obtained from fucose.  
H. W.

**Plant Colloids. VII. Diastase Action.** M. SAMEC (*Koll. Chem. Beihefte*, 1919, 10, 289—304. Compare A., 1914, i, 930; 1915, i, 941).—The processes occurring in the diastatic fermentation of starch have been investigated in the following manner: 10 grams of potato starch were heated with 900 c.c. of water at 120° for half an hour, then cooled to 50° and kept at this temperature, 100 c.c. of 1% diastase solution added, and the reaction allowed to proceed at 50°. At measured intervals of time, 25 c.c. of the reaction mixture were removed and heated rapidly to 100° to stop the action, and then cooled to 25°, at which temperature it was examined. The samples were measured to find, respectively, (i) the molecular weight of the non-dialysable fraction of the products of hydrolysis, that is, the portion with molecular weight greater than 2000—the freezing-point method was used for this purpose; (ii) the colour produced with iodine; (iii) the optical rotation; (iv) the reducing action on Fehling's solution; (v) the

specific conductivity; (vi) the hydrogen-ion concentration; (vii) the velocity of cataphoresis; and (viii) the content of phosphoric acid. The whole of these factors were plotted against the time during which the reaction had been proceeding, and from the curves produced, the following mechanism of the process is deduced. Under the influence of the ferment, the starch molecule decomposes into at least two unequal parts. Of these, one is very like starch in its properties; the other (dialysable) has a somewhat similar structure, since it colours iodine blue. The constitution of the starches and the dextrans appears to be almost analogous, since the optical rotation of both is very similar. The dialysable product possesses marked reducing properties. As the reaction proceeds, the colloidal starch residue separates products of high molecular weight which are more easily dialysable and give a blue iodine reaction. When the molecular weight of the colloidal residue has sunk to below 20,000, the dextrin molecules which separate give a red iodine reaction, and as the process continues they do not give an iodine reaction at all. The initial dextrin products are further decomposed, forming erythro-dextrans and sugar, and the erythro-dextrans pass over into achroo-dextrans. A tabulated scheme of the process, giving molecular weight and iodine reaction at the various stages of the process, is included in the paper.

J. F. S.

**The Acetyl Content of Lignin.** HANS PRINGSHEIM and HANS MAGNUS (*Zeitsch. physiol. Chem.*, 1919, **105**, 179—186).—The author has investigated the origin of the acetic acid produced in the dry distillation of wood and in the processes by which wood and straw are broken down by digestion with alkali. In the latter process, the whole of the acetic acid formed is derived from the lignin substance when the digestion is carried out without heating. If, however, the wood or straw is treated with a solution of sodium hydroxide at the b. p., with or without the use of increased pressure, a small fraction of the acetic acid formed has its origin in cellulose.

The lignin prepared according to the method of Willstätter and Zechmeister (*Zeitsch. angew. Chem.*, 1919, **32**, 41) is not identical with the natural product, since it has undergone hydrolysis and lost its acetyl groups. The natural product may be regenerated by acetylation. The lignin from hornbeam contains nearly double the number of acetyl groups found in lignin from pine-wood.

J. C. D.

**Sulphite Liquors.** KARL H. A. MELANDER (*Tekn. Tidskr.*, 1918, **10**—**12**, pp. 36; from *Chem. Zentr.*, 1919, i. 862—863).—By treatment of sulphite liquor with sodium chloride, the author has obtained a substance which differs considerably in its properties from that prepared by Klason by precipitation with calcium chloride; after purification, it forms a mixture of similar ligninsulphonic acids of high molecular weight in

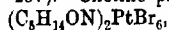
which a portion of the sulphur dioxide is loosely held in ester-like combination. The author designates the mixture *α-lignin-S-acid*, and has shown that the main portion of it is monobasic, whilst only a small part is dibasic. Vanillic acid, protocatechuic acid, and catechol are formed when it is fused with alkali under various conditions. Acetic acid and small amounts of higher fatty acids are also produced, thus pointing to the presence of acetyl groups. The yield of catechol attains 10% of the organic matter of the original substance. Free *α-lignin-S-acid* is obtained as a pale brown powder, which readily becomes resinified when hydrochloric acid is added to the solution of the salted-out product. It is hydrolysed by treatment with alkali. There appears to be little prospect of obtaining the acid in the crystalline condition, since analyses indicate that it is a mixture of relatively complex compounds of almost identical percentage composition. In the *salts* with naphthylamine and toluidine, an atom of nitrogen is present for each atom of sulphur; the latter, however, appears to be present in different forms, partly firmly and partly loosely combined, in the acid. The *sodium* salt is described. The brown colour of *α-lignin-S-acid* renders its titration in the presence of indicators a matter of difficulty. The equivalent, 782, is obtained by titration with sodium hydroxide and determination of the end-point by measurement of the electrolytic conductivity of the solution. Comparison of the potential of the solution against that of a calomel electrode gave the value 882 for another specimen. In certain cases, the use of phenolphthalein was also found possible, and the results show that the presence of an atom of sulphur in the free acid corresponds with that of one ionisable hydrogen atom, so that a carboxyl group cannot be present. The sodium salt is not perceptibly hydrolysed; determinations of the molecular weight in aqueous solution by the freezing-point method gave values between 892 and 991 for different specimens. The electrolytic conductivity of aqueous solutions of the sodium salt at different dilutions has also been determined. H. W.

**Preparation of Butylamine and of *n*-Dibutylamine. The Separation of Aliphatic Amines by Partial Neutralisation.** EMIL ALPHONSE WERNER (T., 1919, 115, 1010—1014).

**Biochemical Formation of Aminoethyl Alcohol from Serine.** F. F. NORD (*Biochem. Zeitsch.*, 1919, 95, 281—285).—Aminoethyl alcohol was isolated from the products of the decomposition of serine by putrefactive bacteria. Ten grams of the amino-acid yielded 2.8 grams of crude aminoethyl alcohol picrolonate.

J. C. D.

**The Muscarine Question. I. Double Salts of certain Bases with Platinum.** ALBERT B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1919, 105, 249—257).—Choline platinibromide,



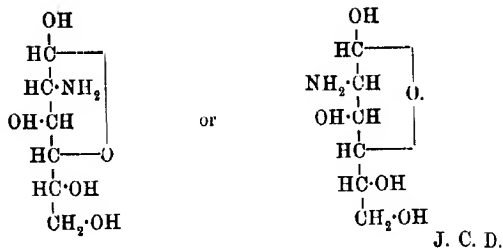
large, dark red prisms or octahedra, m. p. 240° (decomp.), is sparingly soluble in cold water. Choline hydrobromide gives a





A further peculiarity of epichitosamine was found in its behaviour towards nitrous acid. In this case, saccharic acid was obtained, and no dehydration with ring formation followed deamination.

Epichitosamine appears to be an  $\alpha$ -amino-sugar, and there are reasons for believing that it is represented by one of the following formulæ:



***d*-Chondrosamino- and *d*-Chitosamino-heptonic Acids.**  
P. A. LEVENE and I. MATSUO (*J. Biol. Chem.*, 1919, 39, 105—118. Compare Levene, A., 1916, i, 203, 712).—The present communication contains specific directions leading to satisfactory yields of chondrosaminoheptonic acid, and simplified directions for the preparation of chitosaminoheptonic acid. By the action of hydrocyanic acid on hexosamines, a mixture of the two epimerides is obtained. The *d*-chondrosaminoheptonic acids had  $[\alpha]_D^{25} - 3.5^\circ$ . By fractional crystallisation, a levorotatory *d*-chondrosaminoheptonic acid, elongated prisms, m. p.  $139^\circ$  (corr.) (decomp.), and a dextrorotatory *d*-chondrosaminoheptonic acid, were separated. The former showed an original rotation,  $[\alpha]_D^{25} - 8.25^\circ$ , and an equilibrium value of  $[\alpha]_D^{25} - 13.00^\circ$ . This form predominated in the original mixture. *d*-*d*-Chondrosaminoheptonic acid has an initial rotation  $[\alpha]_D^{25} + 42.5^\circ$  and an equilibrium rotation  $[\alpha]_D^{25} + 65.0^\circ$ . The *d*-chitosaminoheptonic acids with original rotation  $[\alpha]_D^{25} + 4.0^\circ$  and equilibrium rotation  $[\alpha]_D^{25} - 1.0^\circ$  were separated into a dextrorotatory *d*-chitosaminoheptonic acid, heavy prisms, m. p.  $192^\circ$  (decomp.), initial rotation  $[\alpha]_D^{25} + 6.5^\circ$  and equilibrium rotation  $[\alpha]_D^{25} + 2.75^\circ$ , and a levorotatory *d*-chitosaminoheptonic acid, prismatic needles, m. p.  $139^\circ$  (corr.) (decomp.), initial rotation  $[\alpha]_D^{25} - 7.5^\circ$  and equilibrium value  $[\alpha]_D^{25} - 12.0^\circ$ . In the original mixture, the dextro-form predominates.

The attempt to isolate the deaminised heptonic acids in a satisfactory condition failed.

After oxidation with nitric acid after deamination, insoluble calcium salts were obtained, which on analysis appeared to be the calcium salts of trihydroxyglutaric acids. The calcium salts obtained from the two acids showed different optical rotation; that from chondrosaminoheptonic acid had  $[\alpha]_D^{25} + 5.0^\circ$  (initial) and  $[\alpha]_D^{25} + 1.5^\circ$  (equilibrium), whilst that from chitosamino-

heptonic acid had  $[\alpha]_D^{25} + 10.0^\circ$  (initial) and  $[\alpha]_D^{25} + 17.0^\circ$  (equilibrium). Theoretically, both aminoheptonic acids should yield the same trihydroxyglutaric acid. J. C. D.

**Constitution of Carbamides. IX. The Interaction of Nitrous Acid and Mono-substituted Ureas. The Preparation of Diazomethane, Diazoethane, Diazo-*n*-butane, and Diazoisopentane from the Respective Nitrosoureas.** EMIL ALPHONSE WERNER (T., 1919, 115, 1093—1102).

**Cyanogen Chloride.** CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1919, 169, 474—476).—There are only two cyanogen chlorides. One, a volatile liquid, has the following constants: m. p.  $-6.5^\circ$ , b. p.  $+12.5^\circ/760$  mm.,  $D_4$  1.222, mean coefficient of expansion ( $0-45^\circ$ ) 0.0019. The other chloride is a solid polymeride, m. p.  $145^\circ$ . The volatile chloride is prepared by the action of chlorine or an acidified solution of sodium hypochlorite on aqueous solutions of hydrogen cyanide, or of equimolecular proportions of sodium cyanide and hydrogen chloride. It is conveniently obtained by the electrolysis of solutions containing equimolecular proportions of hydrogen cyanide and chloride, using a graphite anode in a closed porous pot provided with a delivery tube leading to a freezing bath for the collection of the cyanogen chloride. The porous pot stands in a metal vessel, serving as the cathode, and containing dilute hydrochloric acid. The yield varies from 75 to 80% of the theory. The optimum concentration of the solutions is about 2 gram-mols. per litre, and under these conditions no appreciable hydrolysis of cyanogen chloride by the aqueous hydrochloric acid occurs. The method of Sérullas, namely, the action of chlorine on mercuric cyanide, gives precisely the same product as that obtained by the other methods. G. F. M.

**$\alpha$ ,  $\beta$  and  $\gamma$ -Trinitrotoluenes.** HUGH RYAN and W. M. O'RIORDAN (*Proc. Roy. Irish Acad.*, 1918, 34, 175—193).—The sensitive product to the presence of which accidents with  $\alpha$ -trinitrotoluene are attributed is usually regarded as derived from  $\alpha$ -trinitrotoluene itself, but the assumption that it is derived from the  $\beta$ - or  $\gamma$ -isomeride is equally probable, and would be the more likely if the latter compounds were chemically more reactive than the  $\alpha$ -compound. The behaviour of the three isomerides towards alkalis, amines, hydrocarbons, and aldehydes under comparable conditions has therefore been investigated, and also that of *s*-trinitrobenzene towards alkalis.

The action of aqueous alkali on *s*-trinitrobenzene yields (1) tetranitroazoxybenzene (compare Lobry de Bruyn, A., 1895, i. 653), which exhibits reactions similar to those of Anschütz and Zimmermann's tetranitroazoxytoluene; (2) a small proportion of a compound, m. p.  $200-220^\circ$ , which is possibly hexanitrodiphenyl (m. p.  $234^\circ$ ).

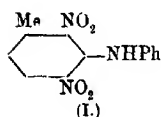
With sodium *n*-butoxide,  $\alpha$ -trinitrotoluene gives a moderately stable compound,  $C_6H_2Me(NO_2)_3 \cdot NaO \cdot C_4H_9$ , which explodes when

dropped into a tube heated at 170°; it is apparently accompanied by a small proportion of a di- or tri-alkyloxide (compare Busch and Kögel, A., 1910, i, 472).

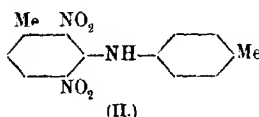
With either alkali hydroxide in presence of an oxidising agent (iodine) or hot alkali hydroxide or carbonate solution,  $\alpha$ -trinitrotoluene gives hexanitrodibenzyl. When treated with alkali hydroxide or carbonate,  $\beta$ -trinitrotoluene yields a dinitro-*m*-cresol, m. p. 101° (compare Will, A., 1914, i, 509), and a large proportion of more complex products, whilst the  $\gamma$ -compound gives, in small amounts, a dinitro-*m*-cresol, m. p. 72–73° (Will, *loc. cit.*), and a crystalline compound insoluble in alkali, possibly a dibenzyl or stilbene derivative. In all cases, dark, amorphous, explosive substances were isolated from the products of the action of alkalis.

$\alpha$ -Trinitrotoluene yields brown, complex compounds under the prolonged action of aqueous ammonia. With alcoholic ammonia, the  $\beta$ -compound reacts readily in the cold, giving  $\beta$ -dinitrotoluidine, m. p. 95–96° (compare Hepp, A., 1883, 315); with aqueous ammonia, the  $\beta$ -compound yields a small proportion of  $\beta$ -dinitrotoluidine, and the  $\gamma$ -compound  $\gamma$ -dinitrotoluidine, m. p. 190–192°.

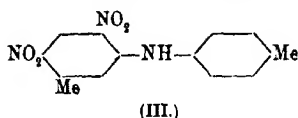
$\alpha$ -Trinitrotoluene forms an additive compound with *p*-toluidine (compare Jackson and Clarke, P., 1906, 83). With aniline,  $\beta$ -trinitrotoluene yields a phenyldinitrotolylamine, m. p. 114–115°, of the probable constitution (I) (compare Hepp, *loc. cit.*), and with *p*-toluidine, a dinitroditolylamine, probably (II), which forms red, prismatic crystals, m. p. 131°. With



*p*-toluidine.  $\gamma$ -trinitrotoluene



With aldehydes in presence of piperidine,  $\alpha$ -trinitrotoluene



condenses, giving (1) with benzaldehyde, 2 : 4 : 6-trinitrostilbene; (2) with anisaldehyde, 2 : 4 : 6-trinitro-4'-methoxystilbene (compare Pfeiffer and Monath, A., 1906, i, 413; 1916, i, 24); and (3) with piperonaldehyde, 2 : 4 : 6-trinitro-3' : 4'-methylenedioxy stilbene,  $C_{15}H_9O_5N_3$ , which crystallises from benzene in dull yellow prisms, turning scarlet on keeping or on being heated, owing to loss of benzene of crystallisation; m. p. (solvent-free), 156–157°. This reaction is not shown by either the  $\beta$ - or the  $\gamma$ -compound, even at 130°, only a brown, amorphous substance being obtained.

With phenanthrene, all three trinitrotoluenes form additive compounds,  $C_{21}H_{15}O_6N_3$ : (1)  $\alpha$ -compound, bright yellow needles, m. p. 98—99°; (2)  $\beta$ -compound, pale yellow, prismatic plates, m. p. 105°; (3)  $\gamma$ -compound, dull yellow, acicular prisms, m. p. 83°.

The four substances examined react differently with alkalis, but in all cases reduction occurs, this probably proceeding to the formation of an amine, the amino-group of which is then replaced by hydroxyl with liberation of ammonia. Complex phenolic compounds are also apparently formed in considerable proportions. In the case of  $\alpha$ -trinitrotoluene, this reduction is accompanied by an oxidation process, yielding hexanitrodibenzyl; non-phenolic compounds obtained from  $s$ -trinitrobenzene and  $\gamma$ -trinitrotoluene may also result from oxidation.

A sample of crude  $\gamma$ -trinitrotoluene was found to contain a dark, amorphous substance, which explodes when heated. T. H. P.

#### $\alpha$ - and $\beta$ -Aminoalkyl(aryl)benzenes and their Derivatives.

A. OGATA (*J. Pharm. Soc. Japan*, 1919, **445**, 193—216).—For the study of the relation between the chemical constitution of amino-compounds and their local narcotic action, the author has prepared (1) five  $\beta$ -aminoalkyl(aryl)benzenes; (2) five  $\alpha$ -aminoalkyl(aryl)benzenes; (3) four aryl derivatives of (1) and (2); (4) two  $\gamma$ -alkylaryl derivatives of (1); and (5) three mixed secondary alkylamines. Primary amines can be prepared from nitriles by reduction with sodium. The author obtained  $\beta$ -phenylethylamine from phenylacetonitrile in 68% yield, and isohexylamine from isohexonitrile.  $\beta$ -Phenylisopropylamine,  $CH_2Ph \cdot CHMe \cdot NH_2$ , can easily be prepared by the action of ammonium formate (2 grams) on benzyl methyl ketone (2 grams) at 180—200°. Similarly were prepared  $\beta$ -aminoisohexylbenzene [ $\beta$ -amino- $\alpha$ -phenyl- $\delta$ -methylpentane],  $CH_2Ph \cdot CH(NH_2) \cdot CH_2Pr^{\beta}$ , b. p. 121°/8 mm. (hydrochloride,  $C_{12}H_{19}N \cdot HCl$ , m. p. 230—231°),  $\beta$ -amino-octylbenzene [ $\beta$ -amino- $\alpha$ -phenyloctane],  $CH_2Ph \cdot CH(NH_2) \cdot [CH_2]_5 \cdot CH_3$ , b. p. 145°/75 mm. (hydrochloride, m. p. 134—136°),  $\alpha\beta$ -diphenylethylamine,  $\alpha$ -phenylethylamine in 65% yield,  $\alpha$ -aminoisohexylbenzene [ $\alpha$ -amino- $\alpha$ -phenyl- $\delta$ -methylpentane],  $NH_2 \cdot CHPh \cdot CH_2 \cdot CH_2Pr^{\beta}$ , b. p. 146°/3 mm. (hydrochloride, m. p. 289°), and  $\alpha$ -aminoheptylbenzene [ $\alpha$ -amino- $\alpha$ -phenylheptane],  $NH_2 \cdot CHPh \cdot [CH_2]_5 \cdot CH_3$ , b. p. 145°/15 mm. (hydrochloride, m. p. 185—186°), from benzyl isobutyl ketone, benzyl  $n$ -hexyl ketone, deoxybenzoin, phenyl isoamyl ketone, and phenyl  $n$ -hexyl ketone respectively.

Secondary amines, such as di- $\beta$ -phenylethylamine, benzyl- $\beta$ -phenylisopropylamine,  $CH_2Ph \cdot NH \cdot CHMe \cdot CH_2Ph$ , b. p. 194°/24 mm. (hydrochloride, m. p. 186.5°), and benzyl- $\beta$ -phenylethylamine have been obtained by reducing with sodium the condensation products of  $\beta$ -phenylethylamine and phenylacetaldehyde, of  $\beta$ -phenylisopropylamine and benzaldehyde, and of  $\beta$ -phenylethylamine and benzaldehyde respectively. iso-*Amylisohexylamine*,  $CH_2Pr^{\beta} \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_2Pr^{\beta}$ , b. p. 208°/758 mm. (hydrochloride, m. p. 258—259°; stannichloride, m. p. 198°), was pre-

pared by the condensation of *iso*amyl bromide and *isohexylamine*, and *isoamylheptylamine*,  $C_{15}H_{27}N$ , b. p.  $229^{\circ}/761$  mm. (*hydrochloride*, m. p.  $235^{\circ}$ ), by the condensation of *iso*amyl bromide and *n*-heptylamine.

Tongue-tests proved that the hydrochlorides of  $\beta$ -amino- $\alpha$ -phenyloctane,  $\alpha\beta$ -diphenylethylamine,  $\alpha$ -phenylethylamine, benzyl- $\beta$ -phenylisopropylamine, and *isoamylisohexylamine* have hypnotic action.

CHEMICAL ABSTRACTS.

**Preparation of Explosives.** THOMAS CAMPBELL JAMES, JAMES IVOR MORGAN JONES, and ROBERT ILLTYD LEWIS (Eng. Pat., 130357).—Trinitrophenylmethylnitroamine (tetryl) forms stable condensation products with aromatic amines, and these can be readily nitrated with warm nitric acid, forming nitro-compounds suitable for use as high explosives. In the case of trinitrophenylmethylnitroamine and aniline, picrylaniline,  $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_5$ , is obtained, and this, when nitrated, yields hexanitrodiphenylamine.

C. A. M.

#### Action of Bromine on some Derivatives of Diphenylamine.

HUGH RYAN and WILLIAM O'RIORDAN (*Proc. Roy. Irish Acad.*, 1919, **34**, 218—225).—The method given by Berger (compare Buisson, "Le Problème des Poudres") for the estimation of the total amount of diphenylamine, either free or as nitroso-derivative, present as stabiliser in a powder, depends on the conversion of the base into its tetrabromo compound. By boiling the powder with dilute sodium hydroxide solution, the diphenylnitrosoamine is converted into diphenylamine; the distillate is then treated with excess of bromine, and the amount not used in the formation of the tetrabromodiphenylamine estimated volumetrically.

The authors' experiments show that the prolonged action of bromine on diphenylnitrosoamine in chloroform solution and in presence of sunlight yields mainly hexabromodiphenylamine, m. p.  $223^{\circ}$  (compare Gnehm, this Journal, 1876, 83), which is also obtained under similar conditions from tetrabromodiphenylamine; the latter represents the first product of the action of bromine on diphenylnitrosoamine.

Since some of the nitro-derivatives of diphenylamine and diphenylnitrosoamine are appreciably volatile in steam, and would hence accompany the diphenylamine in the distillate of Berger's method, the action of bromine on 4-nitro-, 2:10-, and 4:10-dinitrodiphenylnitrosoamines, 2:4-, 2:10-, and 4:10-dinitrodiphenylamines, and 2:4:8:10-tetranitrodiphenylamine has been investigated; of these compounds, the first three and the last have been found among the products of the interaction of diphenylamine with the oxy-acids of nitrogen. With the exception of the tetranitro-compound, all these compounds react with bromine in chloroform solution, the only product being in each case a dibromo-derivative. The derivatives of diphenylnitrosoamine lose the nitroso-group on bromination and yield the same bromo-compounds as the corresponding nitrodiphenylamines.

It is evident that Berger's method (see above), and also that of Dreger (A., 1909, ii, 708), will give untrustworthy results if any of the volatile nitro-compounds formed from diphenylamine in a powder escape interaction with the alkali, or if a mixture of tetra- and hexa-bromodiphenylamines is formed in consequence either of rise of temperature caused by rapid addition of the bromine or of prolonged contact of the bromine with the product.

*Dibromo-4-nitrodiphenylamine*,  $C_{12}H_8O_2N_2Br_2$ , forms bright yellow needles, softening at  $212^\circ$ , m. p.  $216^\circ$ . *Dibromo-2:4-dinitrodiphenylamine*,  $C_{12}H_6O_2N_4Br_2$ , prepared from 2:4-dinitrodiphenylamine, forms orange, rhombic prisms, m. p.  $195.5^\circ$ , and may be identical with the compound, m. p.  $196^\circ$ , obtained by Leymann (A., 1882, 1057). *Dibromo-2:10-dinitrodiphenylamine* forms felted, yellow needles, m. p.  $185-186^\circ$ . *Dibromo-4:10-dinitrodiphenylamine* forms pale yellow needles, m. p.  $247^\circ$ . T. H. P.

#### Action of Nitric Acid and Nitrous Acid on Diphenylamine.

I. HUGH RYAN and PHYLLIS RYAN (*Proc. Roy. Irish Acad.*, 1918 34, 194-204).—The experiments here described were all carried out at the ordinary temperature and at low concentrations. Under these conditions, prolonged interaction of equivalent amounts of diphenylamine and nitric acid in acetic acid solution forms only the nitrate of the base, whilst when a greater proportion of the acid is taken, one portion of the amine is converted into a brown, resinous solid and another portion into nitro-derivatives of diphenylamine, among which the 2:10-dinitro-, 4:10-dinitro-, and 2:4:8:10-tetranitro-derivatives have been identified; in only one experiment was a trace of 2:10-dinitrodiphenylnitrosoamine obtained.

Under similar conditions, the nitration of diphenylnitrosoamine proceeds quite differently. When two or more equivalents of nitric acid are used per one equivalent of diphenylnitrosoamine, the colour of the solution changes slowly from orange to orange-yellow or yellow, with separation of the sparingly soluble 2:10-dinitrodiphenylnitrosoamine. The latter is not formed when only one equivalent of acid is employed, the products then being 4-nitrodiphenylnitrosoamine, and probably a small amount of 2-nitrodiphenylnitrosoamine. When larger proportions of nitric acid are employed, the acetic acid solution is found to contain 2:4:8:10-tetranitrodiphenylamine and 4:10-dinitrodiphenylamine, together with other polynitro-compounds which have not been isolated pure. Three apparently different dinitrodiphenylamines have been prepared; all of these are pale yellow and melt with decomposition. Binary mixtures melting several degrees lower than either of the constituents. The fact that these three compounds lose nitric oxide when heated may have a bearing on the heat tests for nitrocellulose powders stabilised by addition of diphenylamine.

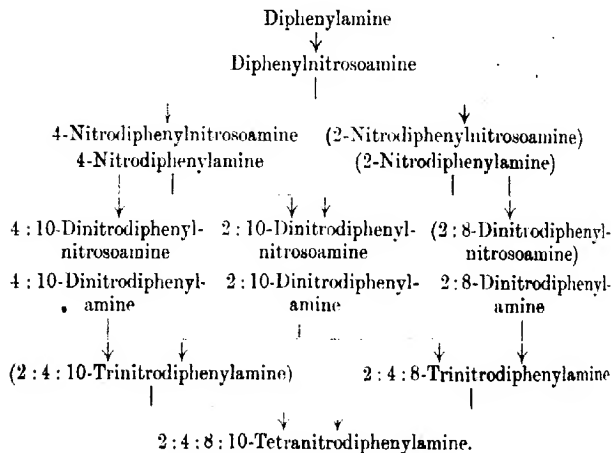
The action of nitric acid on diphenylamine in presence of nitrous acid has also been investigated. In this case, the main product is always a dinitrodiphenylnitrosoamine, the formation of which is

regarded as an indication of the completion of the stabilising action of the diphenylamine.

4:10-Dinitrodiphenylnitrosoamine (?),  $C_{12}H_8O_2N_4$ , obtained by the action in the cold of nitric acid of D 1.43 (6 mols.) on 4-nitrodiphenylnitrosoamine (1 mol.) in glacial acetic acid solution, is a yellowish-white solid, m. p. 155–159° (decomp.) T. H. P.

### Action of Nitric Acid and Nitrous Acid on Diphenylamine.

II. HUGH RYAN and PHYLLIS RYAN (*Proc. Roy. Irish Acad.*, 1919, 34, 212–217. Compare preceding abstract).—Owing to the ease with which the nitroso-group may be split off from nitrodiphenylnitrosoamines, the action of nitric acid on diphenylamine and diphenylnitrosoamine has been examined in the inert solvent, carbon tetrachloride. In this case, the reactions were complicated by separation of the solution into two layers with different relative concentrations of the reacting compounds, but in general the nitrations follow courses similar to those exhibited in acetic acid. Combination of the two sets of results gives the following scheme for the course of the reaction between nitric acid, nitrous acid, and diphenylamine at the ordinary temperature, and at low concentrations of the interacting compounds:



The compounds shown in brackets have not been isolated, but are probably present in some of the fractions obtained. T. H. P.

**Melting Point of Pure Phenol.** HENRI LEROUX (*J. Pharm. Chim.*, 1919, [vii], 20, 88–91).—Pure phenol melts at 40.85° and boils at 182°/760 mm. Phenol is hygroscopic, and the presence of 0.2% of water lowers the melting point to 40°. W. P. S.

**Process for the Preparation of Primary Alcohols.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat., 122630).—Ethylene oxide readily lends itself to the practical synthesis of primary alcohols provided that it is caused to react on an ethereal solution of an aromatic Grignard reagent in the gaseous form at temperatures between  $0^{\circ}$  and  $10^{\circ}$  instead of in ethereal solution at  $-15^{\circ}$ , as hitherto employed. Under these conditions, almost theoretical yields are obtained. Examples are given of the synthesis of phenylethyl alcohol, *p*-tolylethyl alcohol, *p*-methoxyphenylethyl alcohol, and 6-methoxy-*m*-tolylethyl alcohol. [See, further, *J. Soc. Chem. Ind.*, 1919, October.] G. F. M.

**Synthesis of certain Substituted Pyrogallol Ethers, including a New Acetophenetidine derived from the Ethyl Ether of Syringic Acid.** MARSTON TAYLOR BOGERT and JACOB EURLICH (*J. Amer. Chem. Soc.*, 1919, **41**, 798–810).—By conversion of the ethyl ether of syringic acid into the corresponding chloride and amide, and subjection of the latter to the Hofmann reaction, the authors have obtained 3:5-dimethoxyphenetidine, which on acetylation yields 3:5-dimethoxyacetophenetidine; this compound exhibits marked antipyretic properties, and is not more toxic than phenacetin. Syringic acid was obtained in 75% yield from 3:4:5-trimethoxybenzoic acid by a modification of Bogert and Isham's method (*A.*, 1914, i, 532).

3:5-Dimethoxy-4-ethoxybenzoic acid (syringic acid ethyl ether),  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CO}_2\text{H}$ , forms lustrous, white, sword-shaped needles, m. p.  $123-124^{\circ}$  (corr.), and remains apparently unchanged at  $300^{\circ}$ . Its methyl ester,  $\text{C}_{12}\text{H}_{16}\text{O}_5$ , colourless, rhombic plates or long needles, m. p.  $64.5-65^{\circ}$  (corr.), ethyl ester, hexagonal crystals, m. p.  $46-47^{\circ}$  (corr.), b. p.  $195-196^{\circ}/30$  mm., and amide,  $\text{C}_{10}\text{H}_{13}\text{O}_3\cdot\text{CO}\cdot\text{NH}_2$ , white, glistening leaves, m. p.  $154-155^{\circ}$  (corr.), were prepared.

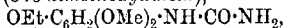
3:5-Dimethoxy-*p*-phenetidine (3:5-dimethoxy-4-ethoxyaniline),  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{NH}_2$ , forms pale brown needles, m. p.  $92-93^{\circ}$  (corr.), and in the air undergoes gradual oxidation to a blue, amorphous substance. In aqueous solution, the amine gives a deep emerald coloration with ferric chloride and spangles of silver with silver nitrate. In concentrated sulphuric acid, it gives a colourless solution, but addition of the solid amine to concentrated nitric acid produces a deep crimson coloration, changing to clear yellow. When diazotised and coupled with  $\alpha$ -( $\beta$ )-naphthol in alkaline solution, the amine yields a deep crimson (bright vermilion) dye.

3:5-Dimethoxyaceto-*p*-phenetidine (3:5-dimethoxy-4-ethoxyacetanilide),  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{NHAc}$ , forms long, white needles, m. p.  $129^{\circ}$  (corr.), and also crystallises with  $\text{H}_2\text{O}$  in white prisms, m. p.  $90^{\circ}$  (corr.); it is not volatile in a current of steam. 2-Bromo-3:5-dimethoxy-4-ethoxyacetanilide,  $\text{C}_{12}\text{H}_9\text{O}_4\text{NBr}$ , was obtained crystalline.

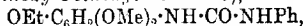
3:5-Dimethoxy-4-ethoxyphenol,  $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{OH}$ , to which the name *homoantiarol* (compare Kiliani, *A.*, 1897, i, 91; Graebe



and Suter, A., 1905, i, 703) is given, forms long, hair-like, pale yellow needles, m. p.  $119^{\circ}$  (corr.), and volatilises slowly even at  $100^{\circ}$ ; it responds to the ordinary reagents for free hydroxyl groups. 1-Iodo-3:5-dimethoxy-4-ethoxybenzene,  $\text{OEt}\cdot\text{C}_6\text{H}_2\text{I}(\text{OMe})_2$ , crystallises in yellow needles, m. p.  $53^{\circ}$  (corr.), and exhibits a powerful odour resembling that of iodoform. 3:5-Dimethoxy-4-ethoxyphenylcarbamide (3:5-dimethoxydulcin),



forms white needles, m. p.  $182^{\circ}$  (corr.), and, unlike dulcin, is practically tasteless. 3:5-Dimethoxy-4-ethoxy-s-diphenylcarbamide (3:5-dimethoxy-4-ethoxycarbanilide),



forms long, white, hair-like needles, m. p.  $185^{\circ}$  (corr.). 3:5-Dimethoxy-4-ethoxybenzeneazo- $\beta$ -naphthol (3:5-dimethoxyphenetidineazo- $\beta$ -naphthol),  $\text{OEt}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ , forms dark red plates with a bronze-like lustre, m. p.  $130^{\circ}$  (corr.), and dyes silk and cotton salmon-pink and wool bright orange, the colours being fast against water, soap, dilute acid, and light. T. H. P.

**Chemical Constituents of Bulbus Scillae.** ERNST BUSCHMANN (*Arch. Pharm.*, 1919, 257, 79—86).—For purposes of investigation, it is essential to use fresh material, since the dried substance contains so much syrupy matter that the extraction of the active principles is practically impossible.

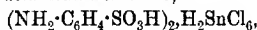
The coarsely powdered material was repeatedly extracted with cold water, and the extracts were treated successively with lead acetate, sodium phosphate, and ethyl acetate; the last removed a small quantity of yellow, crystalline material, the amount of which was too small for further investigation. The presence of choline in the residual aqueous solution was ascertained by the isolation of its platinichloride, m. p.  $241^{\circ}$ , and aurichloride, m. p.  $261^{\circ}$ . The residue left from the treatment with water was extracted with alcohol, and the extract was treated successively with light petroleum (b. p. not above  $50^{\circ}$ ), ether, and chloroform. In this manner, there were obtained (i) xanthoscallide, lemon-yellow needles, m. p.  $117$ — $118^{\circ}$ , which in an impure form constitutes Merck's scillin, scillisterol, m. p.  $163$ — $164^{\circ}$  [acetate, m. p.  $133$ — $134^{\circ}$ ; bromoacetate, m. p.  $196^{\circ}$  (decomp.)], phytosterol, m. p.  $134^{\circ}$  (acetate, m. p.  $125$ — $126^{\circ}$ ), and a brown oil (D 0.9248, iodine number 57.74—60.03, Kötter number 192.65—199.22) in which the presence of formic and palmitic acids, probably also of acetic or propionic acid and oleic acid, was established; (ii) a phytosterol-glucoside, colourless, slender, indistinct needles, m. p.  $290^{\circ}$  (decomp.); and (iii) a small amount of long, slender needles which could not be further investigated.

The aqueous extract which had been treated with lead acetate gradually deposited a brownish-yellow precipitate, from which a strong organic acid was isolated, the investigation of which is not complete; a brown dye was also present. H. W.

**Some Esters of *p*-Nitro- and *p*-Amino-benzoic Acid.** S. V. HINTIKKA and LINDA MELANDER (*Ann. Acad. Sci. Fennicae*, 1919, [A], 10, No. 13; from *Chem. Zentr.*, 1919, i, 836—837).—*Bornyl p-nitrobenzoate*, m. p. 134°, is prepared by heating a mixture of borneol and *p*-nitrobenzoyl chloride. *Camphenilyl p-nitrobenzoate*, needles, m. p. 98°, is similarly obtained from camphenilol (m. p. 68—69°,  $[\alpha]_D +19.12^\circ$ ). *Fenchyl p-nitrobenzoate* crystallises in needles, m. p. 108—109° (the fenchyl alcohol was prepared from fenchone and had  $[\alpha]_D -8.43^\circ$ ). *Bornyl p-aminobenzoate*, prepared by reducing the corresponding nitro-ester with stannous chloride and hydrochloric acid, forms needles or large, regular crystals, m. p. 144°, whilst its *acetyl* derivative crystallises in plates, m. p. 158°. Reduction of camphenilyl *p*-nitrobenzoate leads to a mixture of the amino-ester, plates, m. p. 165°, and a substance, m. p. 126—129°. Attempts to reduce fenchyl *p*-nitrobenzoate by tin or stannous chloride and hydrochloric acid, or by zinc and acetic acid, led to resinous products. The action of hydrogen in the presence of colloidal palladium on an alcoholic solution of the fenchyl ester yielded a product, analyses of which gave results approximating to those required by the formula  $C_{17}H_{23}O_2N$ ; it was an amino-compound, which, however, could not be purified. The ester could not be prepared from a mixture of *p*-aminobenzoic acid, fenchyl alcohol, and concentrated sulphuric acid, which yielded an oil, b. p. 166—168°/10 mm.,  $D_4^{20}$  0.9535,  $n_D^{20}$  1.5193, the formation of which was due to the action of sulphuric acid on the alcohol; it is probably an unsaturated hydrocarbon of high molecular weight. H. W.

**Preparation of Organic Stanno- and Stanni-chlorides.**  
**III. Compounds of the Amino-acids.** J. G. F. DRUCE (*Chem. News*, 1919, 119, 73—74. Compare *ibid.*, 1919, 118, 1, 87).—The following organic derivatives of stannous and stannic chlorides have been prepared and characterised. *Anthranilic acid stannochloride*,  $CO_2H \cdot C_6H_4 \cdot NH_2 \cdot H_2SnCl_3$ , is prepared by warming 1.7 grams of *o*-nitrobenzoic acid with 3.6 grams of granulated tin and 30 c.c. of hydrochloric acid diluted with an equal volume of water. On cooling, after the solution of the tin, the salt separates in colourless, microcrystalline needles, which are washed with diluted hydrochloric acid and dried in the air. The salt softens at 85° and melts at 125° to a colourless liquid. A solution in hydrochloric acid gives a white precipitate with mercuric chloride and a brownish-black precipitate with hydrogen sulphide. This compound has also been prepared by crystallising the component salts together. *Anthranilic acid stannichloride*,  $(NH_2 \cdot C_6H_4 \cdot CO_2H)_2 \cdot H_2SnCl_6$ , is prepared by dissolving 3 grams of the first-mentioned compound in diluted hydrochloric acid and passing a slow stream of chlorine through the solution for three hours. On concentrating, deliquescent needles separate from the solution. This salt was also prepared by crystallising a mixture of the component salts. *m-Aminobenzoic acid stannochloride*,  $(NH_2 \cdot C_6H_4 \cdot CO_2H) \cdot H_2SnCl_4$ , is prepared by an

analogous method to the first-named salt. It crystallises in a mass of feathery needles, m. p.  $240^{\circ}$ ; it is not very soluble in water, but the solution is strongly acid, and boiling does not cause hydrolysis. *m-Aminobenzoic acid stannichloride*,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2 \cdot \text{H}_2\text{SnCl}_6$ , is prepared similarly to the corresponding ortho-compound. It forms short, radiating masses of colourless crystals, m. p.  $193^{\circ}$ . *p-Aminobenzoic acid stannichloride*,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2 \cdot \text{H}_2\text{SnCl}_6$ , may be prepared by crystallising a mixture of the component salts or by reducing *p*-nitrobenzoic acid with tin and hydrochloric acid. Attempts to prepare the corresponding stannochloride yielded only the stannichloride. This compound crystallises in small, pale yellow, brittle needles, and does not melt at temperatures up to  $315^{\circ}$ . *Sulphanilic acid stannichloride*,



is prepared by crystallising a solution of the component salts from hot diluted hydrochloric acid. It forms a white, microcrystalline powder which is sparingly soluble in cold water. With warm water, metastannic acid separates; the salt does not melt, but darkens and decomposes at  $270^{\circ}$ . *4-Aminophthalic acid stannochloride*,



is prepared by reducing 4-nitrophthalic acid with tin and hydrochloric acid. It forms short, white needles, m. p.  $274^{\circ}$ ; it is soluble in cold water, but hydrolysed on heating. *4-Aminophthalic acid stannichloride*,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_3[\text{CO}_2\text{H}]_2)_2 \cdot \text{H}_2\text{SnCl}_6$ , is obtained by warming 2 grams of 4-nitrophthalic acid and 6.9 grams of stannous chloride with 100 c.c. of diluted hydrochloric acid for two hours. It forms small, pale yellow crystals, m. p.  $182^{\circ}$ . *Aminosalicilic acid stannichloride*,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_3[\text{OH} \cdot \text{CO}_2\text{H}]_2)_2 \cdot \text{H}_2\text{SnCl}_6$ , is prepared by reducing nitrosalicilic acid with stannous chloride in alcoholic hydrochloric acid; it forms small, brown, prismatic crystals, m. p.  $128^{\circ}$ . It is soluble in water, but is hydrolysed on warming.

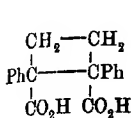
J. F. S.

**Heterocinnamic Acids of Erlenmeyer, jun.** A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 1048—1054).—The author has repeated the experiments of Erlenmeyer by which the heterocinnamic acids were stated to be formed, and is unable to obtain these substances. It would therefore appear that these compounds are not pure substances and cannot be obtained from pure cinnamic acid.

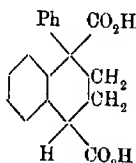
J. F. S.

**Constitution of the isoAtropic Acids.** L. SMITH (*Lunds Univ. Årsskr.*, 1919, [ii], 14, 3—16; from *Chem. Zentr.*, 1919, i, 834—836).—Anhydrous atrolactic acid is smoothly transformed into  $\alpha$ -isoatropic acid when heated at  $140$ — $160^{\circ}$  in an atmosphere of carbon dioxide; at  $200^{\circ}$ , a mixture of the  $\alpha$ - and  $\beta$ -acids, containing about 33% of the latter, is formed. Concentrated alkalis convert the  $\alpha$ -acid into the  $\beta$ -acid. It is therefore possible that the

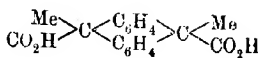
acids are *cis-trans*-isomerides, which is consistent with the formulæ previously proposed for them:



(I.)



(II.)



(III.)

The choice between these formulæ is rendered possible by the fact that the first contains two similarly situated asymmetric carbon atoms; the second has two dissimilar atoms, whilst the third does not possess an asymmetric carbon atom. Since  $\alpha$ - and  $\beta$ -isoatropic acids can be resolved by phenylethylamine, formulæ I and III are excluded. If the acids are really *cis-trans*-isomerides, it should be possible to obtain the active *trans*-form from the active *cis*-form, and this can actually be effected by the action of sodium ethoxide on the *d*- $\alpha$ -acid, whereby the *d*- $\beta$ -acid is produced. The action of alcoholic hydrogen chloride on the  $\alpha$ -acid leads to the formation of a hydrogen ester which, when hydrolysed, yields a mixture of  $\alpha$ - and  $\beta$ -isoatropic acids. The conversion, however, does not occur during esterification, as Liebermann assumed, but during hydrolysis. The hydrogen ester of the  $\alpha$ -acid is an  $\alpha$ -compound which, when hydrolysed in the cold, yields  $\alpha$ -acid mixed with only 10% of the  $\beta$ -isomeride. The hydrogen ester of the  $\beta$ -acid belongs to the  $\beta$ -series, and, contrary to Liebermann's data, cannot be converted by heat or by crystallisation from acetic acid into the  $\alpha$ -isomeride.  $\beta$ -isoAtropic acid and its hydrogen ester yield only  $\beta$ -acid and decomposition products when treated with acetic acid and concentrated hydrochloric acid. Attempts to effect the interconversion by means of ultra-violet light were unsuccessful.

$\alpha$ -isoAtropic acid, m. p.  $238.5-239^\circ$  (corr.), or rather lower when heating is effected too slowly, is best prepared by heating anhydrous atrolactic acid in an atmosphere of carbon dioxide during thirty hours at  $140-160^\circ$ . It is converted by boiling alcoholic sodium ethoxide or aqueous barium hydroxide solution into  $\beta$ -isoatropic acid, m. p.  $208.5-209^\circ$  (corr.). The latter can be resolved into its components with the aid of *l*-phenylethylamine in aqueous-alcoholic solution, when the salt of the *d*-acid separates. *d*- $\beta$ -isoAtropic acid has m. p.  $196.5-197.5^\circ$  (corr.),  $[\alpha]_D + 8.95^\circ$  in alcoholic solution. *l*- $\beta$ -isoAtropic acid, m. p.  $196.5-197^\circ$ ,  $[\alpha]_D - 8.8^\circ$  in alcohol, is similarly obtained by the help of *d*-phenylethylamine. *d*- $\alpha$ -isoAtropic acid, prepared by resolving the *r*-acid with *d*-phenylethylamine, has  $[\alpha]_D + 7.25^\circ$  in alcoholic solution, m. p.  $239^\circ$  after darkening, and softening at  $234^\circ$  when not too slowly heated. *l*- $\alpha$ -isoAtropic acid is isolated from the residues left

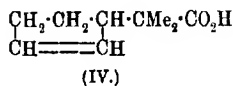
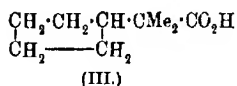
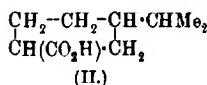
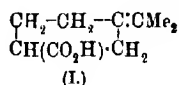
from the separation of the *d*-isomeride or by treatment of the levorotatory mixture of acids which is then produced with *l*-phenyl-ethylamine; it has  $[\alpha]_D - 7.26^\circ$  in ethyl-alcoholic solution. *Ethyl hydrogen  $\beta$ -isotropate* crystallises in plates, m. p.  $116^\circ$  (corr.). *Ethyl hydrogen  $\alpha$ -isotropate* has m. p.  $186^\circ$ . H. W.

**Camphenecamphoric Acid.** S. V. HINTIKKA (*Ann. Acad. Sci. Fennicae*, 1919, [A], 6, iii; from *Chem. Zentr.*, 1919, i, 839—840).—It has been shown previously (A., 1914, i, 409) that carbocamphenilone is formed by the dry distillation of lead hydroxycamphenilinate, and is converted by hydrogen peroxide into

camphenecamphoric acid,  $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H} \\ | \\ \text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2 \end{array}$  (A., 1914,

i, 973). Doubt has been cast on the validity of this formula by Aschan (A., 1914, i, 692), but it may be regarded as established by Lipp's synthesis of the acid (A., 1914, i, 542) and by the complete synthesis of camphenilone (A., 1914, i, 852). The results of further investigations are most readily explained with the help of Lipp's formula. The constitution of carbocamphenilone (annexed

$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CMe}_2 \\ | \quad | \\ \text{CH}_2 \quad \text{CO} \\ | \\ \text{CH}_2-\text{CH}-\text{CO} \end{array}$  formula) follows from its reconversion by sodium hydroxide into hydroxycamphenilanic acid. When camphenecamphoric acid is distilled under ordinary pressure (Aschan, A., 1911, i, 797), it yields a liquid, unsaturated acid,  $\text{C}_9\text{H}_{11}\text{O}_2$ , and an acid,  $\text{C}_{10}\text{H}_{11}\text{O}_3$ , m. p.  $134^\circ$ ; the former probably has the structure (I), since, when reduced with hydrogen in the presence of palladium, it gives an acid,  $\text{C}_9\text{H}_{16}\text{O}_3$ , which appears to be identical with dihydrocamphoceanic acid (II) (Bouveault and Blanc. A., 1908, i, 134; 1909, i, 108; Hintikka, A., 1914, i, 838).



For purposes of comparison, *cyclopentaneisobutyric acid* (III) has been prepared, since the formation of the corresponding unsaturated acid (IV) by the decomposition of camphenecamphoric acid is a possibility. The ketonic nature of the acid,  $\text{C}_{10}\text{H}_{14}\text{O}_3$ , is confirmed by the isolation of a phenylhydrazone; since the acid is converted by cautious heating with potassium hydroxide solution or by boiling with alcoholic sodium methoxide or ethoxide into camphenecamphoric acid, it may be regarded as camphenilone- $\alpha$ -carboxylic

acid (annexed formula). It is probably identical with the acid obtained by Houben and Willfroth (A., 1913, i, 970). The dry distillation of a number of salts of camphenecamphoric acid has been further investigated. The lead salt yields camphenilone, which is also obtained to some extent from the uranyl and ferric salts, but not from the calcium or copper salt.

The following data are recorded. Hydroxycamphenilanic acid has m. p. 176—177°, is optically inactive, and gives camphenilone with lead peroxide and sulphuric acid. The acid,  $C_9H_{16}O_2$ , prepared by reduction of the acid,  $C_9H_{14}O_2$ , has b. p. 138—139°/10 mm., and is stable towards permanganate; the corresponding amide forms leaflets, m. p. 169°. *cyclopentaneisobutyric acid* is a readily volatile oil prepared by the catalytic reduction and subsequent hydrolysis of ethyl *cyclopenteneisobutyrate*; the corresponding amide has m. p. 141—142°, whilst *cyclopenteneisobutyramide* melts at 136—137°. The *phenylhydrazone* of camphenilone- $\alpha$ -carboxylic acid,  $C_{16}H_{20}O_2N_2$ , has m. p. 142—143°. H. W.

**Oxidation of Benzaldoxime.** J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1919, 169, 341—343).—The oximes of the aldehydes which would apparently be formed by the elimination of carbon dioxide from  $\alpha$ -ketonic acids during oxidation with iodine and sodium carbonate do not give on similar treatment the same products of oxidation as the oximes of the  $\alpha$ -ketonic acids themselves. Thus, whilst the oxime of phenylglyoxylic acid gives benzonitrile and diphenylglyoxime peroxide, neither of these substances could be detected among the oxidation products of benzaldoxime. The oxime was treated in benzene solution with aqueous sodium carbonate and iodine. A precipitate of benzaldoxime peroxide,  $CHPh:N \cdot O \cdot O \cdot N:CHPh$ , was formed, and from the benzene layer benzoylbenzaldoxime,  $CHPh:N \cdot OBz$ , and dibenzenyloxazoxime,  $CPh \begin{smallmatrix} NO \\ \diagup \diagdown \end{smallmatrix} CPh$ , were isolated and identified. The latter two substances were separated by forming the easily decomposed iodine additive product of dibenzenyloxazoxime, which is almost insoluble in ether. G. F. M.

**Pungency of Synthetic Aromatic Ketones Related to Zingerone.** LEONORE KLETZ PEARSON (*Pharm. J.*, 1919, 103, 78—80).—The substances are of the type  $CHPh:CH \cdot CO \cdot R$  and  $CH_2Ph \cdot CH_2 \cdot CO \cdot R$ , where one or more hydrogen atoms of the benzene nucleus is replaced by one or more hydroxy- or methoxy-groups, and where R represents the methyl, ethyl, or phenyl radicle. Similar compounds have been studied from the same point of view by Nomura and Nozawa (A., 1918, i, 438); the authors have, however, been able to make several additional generalisations.

The primary, unsaturated condensation products alone, with the exception of *o*-hydroxystyryl methyl ketone, develop no appreciable

pungency on long contact with the tongue; in alcoholic solution, the pungency appears, as a rule, slowly. In the case of the corresponding saturated compounds, the pungency develops quickly, both alone and in alcoholic solution.  $\beta$ -3:4-Methylenedioxyphenylethyl methyl ketone is an exception in that it develops no appreciable pungency by itself. In every case, the unsaturated ketone was much more pungent than the corresponding saturated compound. The replacement of the hydrogen of the phenolic hydroxy-group of zingerone by an acyl radicle appears to have very little effect on the pungency of the compound. On the other hand, 3:4-methylenedioxyethyl methyl ketone and 3:4-methylenedioxyphenylethyl methyl ketone, though containing no free hydroxy-groups, are much more pungent than the corresponding 4-hydroxy-3-methoxy-derivatives, to which they are closely related.

The replacement of the *meta*-hydrogen of the benzene nucleus in *p*-hydroxyphenylethyl methyl ketone by a methoxy-group brings about a decided increase in pungency. The substitution of a bromine atom in this position appears to have a similar effect.

An increase in the weight of the side-chain causes a decided increase in the pungency of the compound. The exceptional pungency of *o*-hydroxyethyl methyl ketone is an outstanding feature of the experiments.

The experimental method of testing the substances consisted in dissolving the compound (0.1 gram) in alcohol (10 c.c.), diluting 1 c.c. of this solution to 3 c.c. or 10 c.c. with water or alcohol (or a mixture), and continuing the dilution in this way until the pungency was found to have become imperceptible. In the case of the more concentrated alcoholic solutions, one or two drops were placed on the tongue; the effect of the alcohol rapidly disappeared, and the pungency became perceptible. With more dilute aqueous solutions, a quantity was taken into the mouth and allowed to remain there for about three seconds.

*4-Hydroxy-3-methoxyethyl methyl ketone*, prepared from vanillin and methyl ethyl ketone, is an almost colourless, crystalline solid, m. p. 94°. *3:4-Dihydroxyethyl methyl ketone* forms pale brown cubes, m. p. 176°. H. W.

### Halogenation of Juglone : New Type of Naphthalene Dyes.

A. S. WHEELER and J. W. SCOTT (*J. Amer. Chem. Soc.*, 1919, 41, 833—841).—Treatment of juglone (5-hydroxy-1:4-naphthaquinone) in acetic acid solution in the cold with chlorine or bromine yields juglone dichloride or dibromide, which loses one molecule of hydrogen haloid under the action of alcohol, giving 2-chloro-(or bromo-)juglone [2-chloro-(or bromo-)5-hydroxy-1:4-naphthaquinone]. In hot acetic acid solution, the action of chlorine on juglone forms 2:3-dichloro-5-hydroxy-1:4-naphthaquinone, whereas that of bromine under similar conditions yields 2:3:8-tribromo-5-hydroxy-1:4-naphthaquinone: both these compounds form acetyl derivatives, and treatment of the tribromo-derivative with alcoholic hydrochloric acid gives 8-chloro-2:3-dibromo-1:4-naphthaquinone.

Further, the 8-bromine atom of the tribromo-compound is replaced by hydroxyl by the action of alcoholic sodium hydroxide, 2:3-dibromo-5:8-dihydroxy-1:4-naphthaquinone resulting.

The tribromojuglone is a brilliant red compound, and constitutes a naphthalene dye of a new type. Its sodium salt, readily prepared by shaking its ethereal solution with aqueous sodium carbonate, is an indigo-blue compound, and dyes silk a fine champagne colour and wool a tan colour, which may be modified by the use of mordants; in both cases, the colour is fast against washing and ironing, and fades only after long exposure to a southern light. Cotton requires a mordant, and, when tannin is used in this capacity, assumes an écreu colour. According to its constitution, juglone itself should act as a dye, but attempts to prepare its sodium salt result in its oxidation, whilst careful halogenation of juglone in the cold yields an unstable additive product.

5-Hydroxy-1:4-naphthaquinone 2:3-dichloride (juglone dichloride),  $C_{10}H_6O_3Cl_2$ , forms lemon-yellow plates, turning brown at  $50^\circ$ , m. p.  $159-160^\circ$ .

2-Chloro-5-hydroxy-1:4-naphthaquinone (2-chlorojuglone),  $C_{10}H_5O_3Cl$ .

forms small, flat, yellowish-brown needles, and emits violet vapour at above  $130^\circ$ , m. p.  $166^\circ$ . Its acetyl derivative,  $C_{12}H_6O_4Cl$ , crystallises in transparent, brownish-yellow plates, m. p.  $147^\circ$ .

2:3-Dichloro-5-hydroxy-1:4-naphthaquinone (2:3-dichlorojuglone),  $C_{10}H_4O_3Cl_2$ , forms lustrous, golden-brown needles, m. p.  $49^\circ$  (dark red liquid); its acetyl derivative,  $C_{10}H_3O_4Cl_2 \cdot OAc$ , forms yellow plates, m. p.  $154^\circ$  (dark brown liquid).

5-Hydroxy-1:4-naphthaquinone 2:3-dibromide (juglone dibromide),  $C_{10}H_6O_3Br_2$ , forms rosettes and fan-shaped groups of yellow, pointed prisms, m. p.  $109^\circ$ .

2-Bromo-5-hydroxy-1:4-naphthaquinone (2-bromojuglone),  $C_{10}H_5O_3Br$ .

forms clusters of translucent, yellowish-brown plates, m. p.  $166^\circ$  (almost black liquid). Its acetyl derivative,  $C_{10}H_4O_4Br \cdot OAc$ , forms golden-brown plates, m. p.  $148^\circ$  (dark yellow liquid).

2:3:8-Tribromo-5-hydroxy-1:4-naphthaquinone (2:3:8-tribromojuglone),  $C_{10}H_3O_3Br_3$ , forms brilliant, deep red needles, m. p.  $170^\circ$ , and dissolves in concentrated nitric or sulphuric acid with a red coloration, and in hot sodium carbonate solution, yielding a purple liquid quickly changing to red. Its sodium derivative,

$C_{10}H_2O_3Br_3Na$ ,

dissolves readily in water or alcohol, and its acetyl derivative,  $C_{10}H_2O_4Br_3 \cdot OAc$ , crystallises in silky, yellow needles, m. p.  $186^\circ$ . Attempts to methylate tribromojuglone were unsuccessful, and oxidation by means of nitric acid or alkaline permanganate solution gave no definite product.

8-Chloro-2:3-dibromo-5-hydroxy-1:4-naphthaquinone (8-chloro-2:3-dibromojuglone),  $C_{10}H_4O_3ClBr_2$ , forms golden-bronze plates, m. p.  $152^\circ$  (dark red liquid).

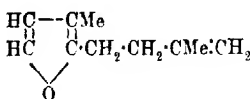
2:3-Dibromo-5:8-dihydroxy-1:4-naphthaquinone (2:3-dibromo-



8-hydroxyjuglone),  $C_{10}H_4O_4Br_2$ , forms small, golden-brown, prismatic needles, and emits vapour at about  $160^\circ$ , m. p.  $236^\circ$  (black liquid). T. H. P.

**Solubility of Camphor in Water.** H. LEO and E. RIMBACH (*Biochem. Zeitsch.*, 1919, **95**, 306—312).—The solubility of camphor in water at the ordinary temperature is 1 in 598. In Ringer's solution under the same conditions, it is 1 in 577. The solubility falls with rise in temperature. The dissolution of camphor in water is an exothermic process. J. C. D.

**Essential Oil of Perilla citriodora, Makino.** HEISABURO KONDO and SEITARO YAMAGUCHI (*J. Pharm. Soc. Japan*, 1919, **446**, 263—275).—*Perilla citriodora*, Makino, which belongs to the *Labiatae* group, is known to contain an essential oil in an amount 2—3% of the weight of the dry leaf, having D 0.911—0.913; 59.26% of the oil is citral. The authors have investigated the chemical nature of the remaining portion of the oil after the citral is removed. This oil, after being dried over calcium chloride, can be distilled into five fractions under 25 mm. pressure: (1)  $90-100^\circ$ , 49%; (2)  $100-120^\circ$ , 5%; (3)  $120-130^\circ$ , 9%; (4) above  $130^\circ$ , 6%; (5) residue, 31%. From the first fraction they have isolated a substance which they have named *perillen*, b. p.  $185-186^\circ$ ,  $D^{20}_D$  0.9017,  $n^{20}_D$  1.47053,  $[\alpha]_D$  zero. Analysis gives the empirical formula  $C_{16}H_{14}O$ . There are only a few substances known to occur in plants having a similar composition, the best known being carvone and myrrol. *Perillen* differs from the former in b. p. and odour, and from the latter by the fact that the purple colour with bromine quickly changes to green. It contains one furan nucleus, one methyl group, and one side-chain with one double bond, which on oxidation yields  $CH_3Pr^{\beta}CH_2CO_2H$ . The annexed formula is suggested for this new oil. *Dihydroperillen* is obtained by reducing *perillen*, b. p.  $182^\circ$ ,  $D^{22}_D$  0.8852,  $n^{22}_D$  1.45762. From the remaining fractions there was obtained a compound, b. p.  $251^\circ$ ,  $D^{11}_D$  0.9088,  $n^{11}_D$  1.50176,  $[\alpha]_D$   $-4.358^\circ$ , which is concluded to be a sesquiterpene.



#### CHEMICAL ABSTRACTS.

**Uzarin from Gomphocarpus Root.** LUDWIG KOFLER (*Arch. Pharm.*, 1917, **255**, 550—552).—Uzarin (compare Hennig, A., 1918, i, 94) may be readily obtained by extracting the root known as *Gomphocarpus spec.*, or Wasicky's ithongua (*Ber. deut. Pharm. Ges.*, 1916, **26**, 267), with methyl alcohol on the water-bath, evaporating the alcohol, treating the residue with boiling water, filtering the hot solution, and recrystallising the uzarin which separates on cooling, first from a mixture of methyl alcohol and ether, and afterwards from boiling water. The percentages of uzarin obtained in this way from the two products were 4.84 and 3.70 respectively. Uzarin has a slightly bitter taste, and is pre-

precipitated from aqueous solution by tannic acid, excess of which redissolves the precipitate. Various colour reactions of the glucoside are described. It begins to decompose at  $190^{\circ}$ . T. H. P.

**Meconic Acid and its Behaviour in the Estimation of Morphine in Opium.** A. HEIDUSCHKA and M. FAUL (*Arch. Pharm.*, 1917, 255, 482—496).—Ammonium meconate separates in crystals containing  $1\text{H}_2\text{O}$  when prepared in aqueous solution or in the anhydrous form,  $(\text{NH}_4)_2\text{C}_7\text{H}_3\text{O}_7$ , when prepared from meconic acid and ammonium acetate in absolute alcoholic solution; the salts are neutral towards iodeosin and dimethylaminoazobenzene. Calcium meconate has the formula  $\text{C}_7\text{H}_2\text{O}_7\text{Ca}$ , or, when dried at  $110^{\circ}$ ,  $\text{C}_{14}\text{H}_2\text{O}_{13}\text{Ca}_2$ , both salts being neutral towards the above indicators; the solubility of the former in  $N/10$ -ammonia solution was measured at  $18^{\circ}$ .

The meconic acid contained in opium does not affect the results obtained in estimating the morphine by precipitation with ammonia (compare this vol., ii, 437). T. H. P.

**Physiologically Active Constituents of Certain Philippine Medicinal Plants. III.** A. H. WELLS (*Philippine J. Sci.*, 1919, 14, 1—7).—The dry wood of *Arcangelisia flava* (Linn.) contains 4.8% of berberine, probably a higher percentage than that in any other Philippine plant. As the wood is soft and porous and contains but little extractive matter, the recovery of the alkaloid is simple, involving merely maceration with 95% alcohol, evaporation of most of the alcohol, and the recrystallisation of the salt formed by the addition of a mineral acid to the concentrated liquor. The plant is therefore an excellent source of the drug. *Cassia siamea* (Lam.) occurs only in cultivation as a shade tree. The pods, leaves, and branches contain a poisonous alkaloid having the empirical formula  $\text{C}_{14}\text{H}_{19}\text{O}_3\text{N}$ . The rhizomes of *Geodorum nutans* contain about 14% of a water-soluble adhesive gum of exceptional strength and lasting power. *Coriaria intermedia*, known in New Zealand as "toot plant," contains small quantities of a poisonous glucoside in its leaves and fruit. G. F. M.

**Syntheses in the Cinchona Series. I. The Simpler Cinchona Alkaloids and their Dihydro-derivatives.** MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1919, 41, 817—833).—The reduction products of various cinchona alkaloids and certain synthetic homologues of these products are described. The reduction of cinchonine, cinchonidine, quinine, and quinidine to hydrocinchonine, hydrocinchonidine, hydroquinine, and hydroquinidine was readily effected by means of palladium chloride in dilute sulphuric acid solution (D.R.-P. 252136). The properties of the hydrogenated alkaloids obtained agree with those recorded for the natural compounds. Hydrocupreine may be prepared in large quantity by de-etherifying hydroquinine by means of boiling aqueous hydrobromic acid.

Hydrocupreine and its ethyl ether, which, as derivatives of hydro-

quinine, are levorotatory, are compared with the corresponding dextrorotatory stereoisomerides derived from hydroquinidine. These, which are named hydrocupreidine and ethylhydrocupreidine, have not been previously described, although the former was evidently obtained crystalline by Forst and Böhringer (A., 1882, 1306) by heating hydroquinidine with hydrochloric acid in a sealed tube. Hydrocupreidine is readily isolated from hydroquinidine by the method used for preparing its levorotatory isomeride, hydrocupreine, and it is easily converted into its ethyl ether by means of ethyl sulphate and alcoholic alkali.

Quinine was prepared by isomerisation of quinidine in accordance with Miller, Rohde, and Fussenegger's instructions (A., 1901, i, 95), and was readily isolated in good yield as the monohydrochloride, which was unobtainable by other workers.

*sec*-Octylhydrocupreine dihydrochloride, recommended in Germany during the war, under the name "Vuzin," for the treatment of infected wounds, has also been prepared by the authors.

The values given for the optical rotations are calculated from the formula  $[\alpha] = 100a/lc$ ,  $c$  representing grams of substance per 100 c.c. of solvent; for low concentrations, these values are close approximations to the true ones.

The properties of the anhydrous hydrochlorides of the bases are as follows: cinchonine, softens at  $175^{\circ}$ , m. p.  $217-218^{\circ}$  (slow decomp.),  $[\alpha]_D^{25} + 177.4^{\circ}$  ( $c = 1.083$ ); cinchonidine, softens at about  $160-170^{\circ}$ , m. p.  $242^{\circ}$  (slow decomp.),  $[\alpha]_D^{20} - 117.6^{\circ}$  ( $c = 1.214$ ); quinine, melts to a jelly at  $154-160^{\circ}$ ,  $[\alpha]_D^{20} - 149.8^{\circ}$  ( $c = 1.322$ ); quinidine, m. p.  $258-259^{\circ}$  (decomp.) with previous darkening and sintering,  $[\alpha]_D^{20} + 200.8^{\circ}$  ( $c = 1.3$ ); hydroquinidine, m. p.  $206-208^{\circ}$ ,  $[\alpha]_D^{20} - 123.9^{\circ}$  ( $c = 1.113$ ); hydrocinchonidine, m. p.  $202-203^{\circ}$ ,  $[\alpha]_D^{20} - 89.4^{\circ}$  ( $c = 1.197$ ).

Hydrocupreine, prepared as described above, forms faintly cream-coloured plates, and at  $185-190^{\circ}$  swells and evolves gas, with formation of an adherent, glassy mass, which liquefies completely and darkens at  $230^{\circ}$ ;  $[\alpha]_D^{20} - 148.7^{\circ}$  ( $c = 1.13$ ) (compare Giemsa and Halberkann, this vol. i, 33). The hydrochloride,  $C_{19}H_{24}O_2N_2.HCl$ , forms anhydrous, radiating masses of needles, blackening at above  $255^{\circ}$ , m. p.  $280^{\circ}$  (decomp.; rapid heating),  $[\alpha]_D^{25} - 132.3^{\circ}$  ( $c = 0.945$ ). The dihydrobromide ( $+ 2H_2O$ ) forms leaf-like aggregates of irregular prisms; the anhydrous salt turns yellow and softens to a jelly at about  $180-190^{\circ}$ , gradually liquefying at higher temperatures. The nitrate forms rosettes of anhydrous, flat needles, m. p.  $220-222^{\circ}$  (darkening).

Ethylhydrocupreine hydrochloride (compare Giemsa and Halberkann, *loc. cit.*) forms anhydrous, rhombic crystals melting at  $252-254^{\circ}$  to a brown, turbid liquid, which rapidly clears,  $[\alpha]_D^{25} - 123.6^{\circ}$  ( $c = 0.959$ ). The hydrobromide forms aggregates of anhydrous rhombs, m. p.  $258-259^{\circ}$  (darkening), the dihydrobromide ( $+ 0.5H_2O$ ), greenish-yellow crusts of rhombic crystals, and the methiodide, glistening, pale yellow plates, m. p.  $195-196^{\circ}$ ,  $[\alpha]_D^{25} - 113.0^{\circ}$  ( $c = 0.992$ ).

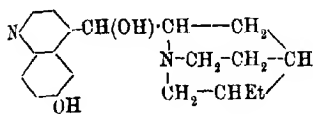
*sec*-Octylhydrocupreine dihydrochloride ("vuzin") forms pale

yellow sheaves and rosettes of slender needles ( $+2\text{H}_2\text{O}$ ); the anhydrous salt softens slightly above  $140^\circ$ , melts to a jelly at  $157\text{--}160^\circ$ , and liquefies completely at  $190\text{--}195^\circ$  (evolution of gas).

Hydrocinchonine hydrochloride was prepared (1) from the alkaloid occurring naturally as a by-product in the oxidation of commercial cinchonine to cinchotennine, and (2) from the base prepared by reducing cinchonine by means of palladium and hydrogen. Both salts ( $+2\text{H}_2\text{O}$ ) conformed to Forst and Böhringer's description (A., 1881, 620). Anhydrous salt (1) darkens above  $180^\circ$ , m. p.  $220-221^\circ$ ,  $[\alpha]_D^{25} + 155.2^\circ$  ( $c=0.796$ ), whilst (2) darkens slightly above  $200^\circ$ , m. p.  $221-223^\circ$  (evolution of gas),  $[\alpha]_D^{25} + 159.3^\circ$  ( $c=0.741$ ) (compare von Arlt, A., 1899, i, 962).

Hydroquinidine hydrochloride (compare Forst and Böhringer, A., 1882, 1306) darkens at about 270° and decomposes at 273—274°,  $[\alpha]_D^{25} + 183.9^\circ$  ( $c = 1.278$ ).

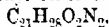
*Hydrocupreidine* (annexed formula) forms glistening, cream-coloured, hexagonal plates (+0.5—1H<sub>2</sub>O); the anhydrous base



softens to a jelly above 170° and liquefies completely at about 195°,  $[\alpha]_D^{25} + 253.4^\circ$  (in alcohol;  $c=1.422$ ). In its chemical properties it is strictly analogous to its levorotatory stereoisomeride.

The *hydrochloride*,  $C_{19}H_{22}O_2N_2 \cdot HCl \cdot H_2O$ , forms rosettes and sheaves of prismatic needles, and, when anhydrous, has m. p. 231–233° (darkening),  $[\alpha]_D^{24} + 194.2^\circ$  ( $c = 0.618$ ); its aqueous solution is yellow. The *dihydrobromide* forms anhydrous, pale yellow, glistening plates, and turns yellow when heated, but does not melt at 275°. The *hydriodide* forms pink, rhombic plates ( $+ H_2O$ ), m. p. 209–212° (anhydrous). The *nitrate* forms cream-coloured rhombs ( $+ H_2O$ ), the anhydrous salt turning yellow and softening to a jelly at about 160°, and liquefying completely at 175–180°. The *methiodide* forms glistening prisms, m. p. about 295° (decomp.),  $[\alpha]_D^{20} + 202.6^\circ$  (in 50% alcohol;  $c = 0.555$ ).

*Ethylhydrocupreidine* (ethyl ether of hydrocupreidine).



forms rosettes and sheaves of slender needles, m. p. 197.5–198°, showing slight preliminary softening and resolidifying a few degrees below the melting point;  $[\alpha]_D^{25} + 212.8^\circ$  (in alcohol;  $c = 1.008$ ). The *hydrochloride* forms nacreous aggregates of flat needles and long, narrow plates ( $+4H_2O$ ) with a slightly bitter taste; the anhydrous salt sinters to a jelly at 140–155°, m. p. 258–260°,  $[\alpha]_D^{25} + 183.3^\circ$  ( $c = 0.592$ ). The *hydrobromide* forms anhydrous, rhombic crystals, m. p. 250.5–253° (slow decomp.). The *dihydrobromide* forms radiating masses of slender, silky needles ( $+0.5H_2O$ ), the dried salt turning yellow above 130°, melting to a jelly at about 175–185°, and swelling and evolving gas at 200–205°. The *methiodide* forms rhombs and prisms, decomposing at 253–255°,  $[\alpha]_D^{25} + 189.6^\circ$  (in methyl alcohol;  $c = 1.131$ ).

Quinicine hydrochloride,  $C_{20}H_{24}O_2N_2 \cdot HCl$ , which may readily be

prepared directly from the base, forms arborescent aggregates of minute leaflets, m. p. (1) 179—180°, (2) 180—182°,  $[\alpha]_D^{25}$  (1) +16.26° ( $c=0.80$ ), (2) +13.7° ( $c=1.861$ ). T. H. P.

**Stereochemistry of Hyoscine.** HAROLD KING (T., 1919, 115, 974—982).

**Preparation of 6-Hydroxy-2-phenylpyridine-5-carboxylic Acid.** CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.P. 312098; from *Chem. Zentr.*, 1919, ii, 852).—The process depends on the oxidation of 2-phenylquinoline bases, substituted in the benzene nucleus, by potassium permanganate in acid solution. Examples are cited of the oxidation of 8-methoxy-2-phenylquinoline, 8-hydroxy-2-phenylquinoline, 6-ethoxy-2-phenylquinoline, m. p. 132° (prepared by heating the corresponding 4-carboxylic acid at 250°), and 6-amino-2-phenylquinoline, m. p. 122—123° (prepared by heating the corresponding 4-carboxylic acid above its melting point). 6-Hydroxy-2-phenylpyridine-5-carboxylic acid (2-phenylpyridone-5-carboxylic acid) forms colourless crystals, m. p. 280—281° (corr.), 287—288° when rapidly heated, and is transformed at 300° into 2-phenylpyridone. A sulphonic acid is produced when it is treated with sulphuric acid containing 15% of SO<sub>3</sub> at 150—160°. The aqueous solutions of the alkali salts are slightly fluorescent. The acid is used medicinally. 6-Hydroxypyridine-2:5-dicarboxylic acid, m. p. 287—289° (decomp.), is obtained as a by-product during the oxidation of 8-methoxy-2-phenylquinoline. H. W.

**Dyes Derived from Quinolinic Acid.** PRAPHULLA CHANDRA GHOSH (T., 1919, 115, 1102—1105).

**Crystallography and Optical Properties of Pinaverdol.** EDGAR T. WHERRY and ELLIOT Q. ADAMS (*J. Washington Acad. Sci.*, 1919, 9, 396—405).—Pinaverdol, or 1:1':6'-trimethylisocyanine iodide, is used as a sensitising dye for photographic plates. The crystals are monoclinic ("peri-rhombic") with  $a:b:c=1.1014:1.16053$ ,  $\beta=88^\circ 20'$ , and they vary from prismatic to tabular in habit in different preparations. They display brilliant reflection pleochroism with metallic colours; faces in the prism-zone are brass-yellow, whilst those nearly perpendicular to the vertical axes are bronze-violet; faces lying between these display intermediate colours, usually a brilliant metallic-green (beetle-green). Crystals less than 0.02 mm. in thickness transmit light and show strong absorption and pleochroism. Refractive indices,  $\alpha$  about 1.58,  $\beta$  and  $\gamma$  more than 1.75, probably near 2.0; optically negative.

L. J. S.

**Isolation of the Iodine Compound which Occurs in Thyroid.** E. C. KENDALL (*J. Biol. Chem.*, 1919, 39, 125—147).—Hydrolysis of the fresh thyroid glands is effected with aqueous sodium hydroxide for twenty-four hours. A quantitative separation

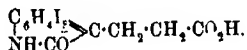
the fate as sodium soaps is then possible, and a perfectly clear alkaline filtrate of the hydrolysed tissue is obtained. On acidification of this solution, a fine, flocculent precipitate separates which contains approximately 26% of the total iodine. The total iodine is therefore divided into acid-soluble and acid-insoluble fractions. The proportion found in each fraction is remarkably constant, and it is suggested that the ratio expresses the equilibrium existing in the glands between the completed iodine compound possessing physiological activity and the materials which are used by the gland in the building up of this substance. When physiologically tested, the acid-soluble components are inactive, but the small acid-insoluble fraction is highly active.

This fraction apparently consists of a mixture of substances possessing the properties of colloids. As a whole, the fraction possesses acidic properties, and it was ascertained that the iodine compound was not present in the free form. By repeated precipitation with barium hydroxide and removal of the barium as barium sulphate, a preparation containing 47.3% of iodine and nearly free from coloured impurities was obtained. This material was dissolved in 95% alcohol, and on evaporation yielded a white powder insoluble in alcohol and containing about 60% of iodine. When this product was dissolved in aqueous sodium hydroxide, precipitated by adding sulphuric acid, and boiling, it was converted into fine, white, microscopic crystals. This iodine compound has been termed *thyroxin*. The experimental conditions which influence the isolation of thyroxin are fully considered. When an impure preparation of thyroxin is neutralised, iodine is eliminated, but this does not occur as readily when the pure product is used. Thyroxin is very susceptible to reduction in alkaline solution by means of metals.

There are two distinct actions produced by carbon dioxide. One is a partial purification of thyroxin by precipitation from an alkaline solution, whilst the other results in the formation of a mono-metal salt of the closed-ring form of thyroxin.

One of the most important reasons for the failure to separate thyroxin consistently was the variability of the samples of desiccated thyroid used. Samples obtained during the winter months show that during this period the glands are so low in iodine content as to make the isolation impracticable.

The process has been carried out on a large scale, and is fully described. It is stated that the substance is  $\beta$ -4:5:6-tri-iodo-2-keto-4:5:6-trihydroindolepropionic acid,



It may exist in three forms, a keto-form with the carbonyl group adjacent to the imino-group, the tautomeric form with an  $\alpha$ -hydroxy-group and doubly linked nitrogen with no hydrogen in position 1, and a form in which there is an open-ring structure. It is stated that the synthesis has been accomplished by Osterberg

in 1917, and that his work has been repeated and confirmed in 1919. No details of the synthesis or of the determination of structure are given.

An acetyl derivative has been prepared. This derivative yielded a disilver salt, and to account for this, rupture of the pyrrole ring between the imino- and the carbonyl groups is assumed to have taken place.

J. C. D.

**Capsaicin.** I. ARTHUR LAPWORTH and FRANK ALBERT ROYLE (T., 1919, 115, 1109—1116).

**Preparation of Nitrogenous Condensation Products of the Anthraquinone Series.** FARBERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 311906; additional to D.R.-P. 298706; from *Chem. Zentr.*, 1919, ii, 851—852. Compare A., 1918, i, 191).—Thiazole compounds are obtained by treating *o*-halogen-substituted acetylaminanthraquinones with alkali sulphides in accordance with the scheme  $A \begin{smallmatrix} \text{NH} \cdot \text{CO} \cdot \text{R} \\ \text{Hal} \end{smallmatrix} + \text{H}_2\text{S} \rightarrow A \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{R} + \text{H}_2\text{O} + \text{H} \cdot \text{Hal}$ .

where A represents the anthraquinone group. Thus, *C-phenyl-1:2-anthraquinonethiazole*, pale brown needles, which yield yellow to reddish-brown solutions in organic solvents and yellowish-brown solutions in sulphuric acid, is prepared by boiling 2-bromo-1-benzoylaminoanthraquinone with alcohol and crystalline sodium sulphide. Similarly, 1-chloro-2-acetylaminoanthraquinone gives *C-methylantraquinone-2:1-thiazole*, yellowish-green needles, m. p. 258°, which dissolve in organic media and sulphuric acid, forming yellowish-brown and yellow solutions respectively.

H. W.

**Reaction of Iodoantipyrine.** J. BOUGAULT (*Ann. Chim. anal.*, 1919, [ii], 1, 254; from *Soc. Pharm.*, 1919).—Two atoms of iodine are liberated, and antipyrine (1-phenyl-2:3-dimethyl-5-pyrazolone) is regenerated when an aqueous solution of iodoantipyrine is treated with potassium iodide and hydrochloric acid; this reaction, analogous to that given by hypiodous amides, indicates that the iodine is combined directly with the nitrogen, although this is not confirmed by the formula ascribed to the substance. W. P. S.

**Pyrimidines. LXXXVII. Alkylation of 5-Aminouracil.** TREAT B. JOHNSON and IWAO MATSUO (*J. Amer. Chem. Soc.*, 1919, 41, 782—789).—It has been shown that exhaustive alkylation by means of methyl iodide converts uracil and 5-nitrouracil ultimately into the corresponding 1:3-dimethylpyrimidines. 5-Aminouracil offers, however, greater possibilities of substitution than either of these pyrimidines owing to the presence of the basic amino-group in the 5-position of the ring. Experiment shows that the potassium salt of the aminouracil reacts with methyl iodide at the temperature of boiling methyl alcohol, yielding 5-amino-1:3-dimethyluracil, the substitution occurring entirely in the nucleus of the pyrimidine ring. That substitution does not take place in the

amino-group is established by the fact that, of the four nitrogen-substituted dimethyl derivatives possibly obtainable by alkylation with methyl iodide, neither 5-dimethylaminouracil (compare Wheeler and Jamieson, A., 1904, i, 942) nor 5-methylamino-1-methyluracil nor 5-methylamino-3-methyluracil (see below) is identical with the compound actually obtained.

In the conversion of uracil into 5-nitrouracil, the large excess of nitric acid (D 1.5) is now found to be unnecessary, a theoretical yield being obtained with 4.5 parts of the acid per 1 part of uracil.

5-Amino-1 : 3-dimethyluracil,  $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NH}_2$ , forms hexagonal plates, m. p. 233–235°, its *hydriodide*, colourless prisms, m. p. 275°, and its *picrate*, yellow needles, melting at 246° to a dark oil with marked effervescence.

5-Methylamino-1-methyluracil,  $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHMe}$ , obtained from 5-bromo-1-methyluracil and methylamine, forms needles, m. p. 209°, and responds to Wheeler and Johnson's test for uracil (A., 1907, ii, 826); its *picrate* crystallises in long, yellow needles, m. p. 175°.

Alkylation of 2-ethylthiol-6-pyrimidone with methyl iodide under the conditions employed by Johnson and Heyl (A., 1907, i, 728) for the preparation of 2-ethylthiol-1-methyl-6-pyrimidone, followed by hydrolysis by digestion with hydrochloric acid, yields a mixture of uracil, 1-methyluracil, and 3-methyluracil, so that alkylation occurs in both the 1- and 3-positions.

5-Bromo-3-methyluracil, prepared by Johnson and Clapp (A., 1908, i, 835) by the action of bromine on aqueous 3-methylcytosine, may also be obtained in quantitative yield by treatment of 3-methyluracil with bromine in glacial acetic acid solution at the ordinary temperature.

5-Methylamino-3-methyluracil,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHMe}$ , prepared by heating 5-bromo-3-methyluracil with excess of aqueous methylamine solution (33%), forms plates, m. p. 206°.

5-Methylaminouracil,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHMe}$ , obtained by heating 5-bromouracil (1 mol.) with 33% aqueous methylamine (4 mols.) solution, forms crystals, and, when heated slowly, gradually decomposes without melting; when heated rapidly, it darkens at 285° and melts with violent effervescence at 297°. It gives Wheeler and Johnson's reaction for uracil. Its *picrate* forms stout prisms, m. p. 185° (efferves.).

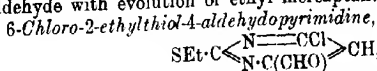
An attempt to prepare 5-amino-1 : 3-dimethyluracil from 5-nitro-1 : 3-dimethyluracil by reduction with aluminium amalgam in dilute aqueous ammonia gave unsatisfactory results.

T. H. P.

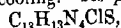
**Pyrimidines. LXXXVIII. Synthesis of Cytosine Aldehyde.**  
 HAT B. JOHNSON and LOUIS A. MIKESKA (*J. Amer. Chem. Soc.*, 1919, 41, 810–817).—The action of phosphorus oxychloride or



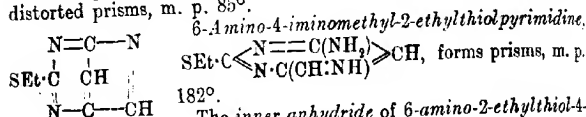
pentachloride on 2-ethylthiol-4-aldehydo-6-pyrimidone (compare Johnson and Cretcher, A., 1915, i, 1002) gives, not the expected imide chloride or its chloro-ether, but 6-chloro-2-ethylthiol-4-aldehydopyrimidine. The action of ammonia on this compound results in the replacement of the chlorine atom by an amino-group, but the ammonia reacts also with the aldehyde group, giving 6-amino-4-iminomethyl-2-ethylthiopyrimidine; hydrolysis of the latter appears to proceed beyond the formation of cytosine-4-aldehyde to the stage of complete reduction of the compound to uracil. A third product of the action of alcoholic ammonia on 6-chloro-2-ethylthiol-4-aldehydopyrimidine is the anhydro-derivative of 6-amino-2-ethylthiol-4-aldehydopyrimidine, this resulting from the inner condensation of the corresponding aldehyde. The 6-amino-2-ethylthiol-4-aldehydopyrimidine was not isolated, but it appears to represent the principal product of the reaction, and, on digestion with hydrochloric acid, is converted into cytosine-4-aldehyde with evolution of ethyl mercaptan.



forms a dark oil, b. p. 138—139°/10 mm., 151—158°/14 mm., solidifying completely on cooling. Its *phenylhydrazone*,



forms long, yellow needles, m. p. 147°, and its *anil*,  $\text{C}_{13}\text{H}_{12}\text{N}_3\text{ClS}$ , distorted prisms, m. p. 85°.



The inner anhydride of 6-amino-2-ethylthiol-4-aldehydopyrimidine (annexed formula) forms crystals, m. p. about 210° (decomp.).  
 T. H. P.

**Ricinine.** E. WINTERSTEIN, J. KELLER, and A. B. WEINHAGEN (*Arch. Pharm.*, 1917, 255, 513—539).—The formula,  $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_6$ , given by Soave (A., 1896, i, 386) for ricinine must be regarded as erroneous, the results of the authors' analyses and of an investigation of the decomposition products indicating the formula  $\text{C}_8\text{H}_5\text{O}_2\text{N}_3$ , although ebullioscopic measurements in chloroform, methyl acetate, and pyridine yield values corresponding with  $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}_3$ ; no explanation of this discrepancy is advanced. The compound,  $\text{C}_8\text{H}_5\text{O}_2\text{N}_3\cdot\text{HgCl}_2$ , m. p. 201—202°, Soave (*loc. cit.*) described as  $\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}_3\cdot 2\text{HgCl}_2$ , m. p. 204°.

Ricinine is readily hydrolysed by alkalis, yielding methyl alcohol and the sparingly soluble ricinic acid,  $\text{C}_7\text{H}_4\text{O}_2\text{N}_3$ , m. p. 292°. Soave gave m. p. 295°, and Maquenne and Philippe (A., 1904, i, 339; 1905, i, 80) m. p. 320°, which is that of the sodium salt. One hundred grams of water dissolve 0.072 gram of the acid at 18° and 0.87 gram at 100°. The silver (+  $\text{H}_2\text{O}$ ) and barium salts were prepared and analysed. Ricinic acid is optically inactive.

and attempts to esterify it were unsuccessful. Treatment of ricinine with a small proportion of permanganate results in hydrolysis accompanied by oxidation of the methyl alcohol liberated, whilst, when excess of permanganate is used, ammonia, hydrocyanic, oxalic, and succinic acids are formed, together with other products not investigated.

When distilled with zinc dust, ricinine gives pyridine and other compounds, and when fused with potassium hydroxide, aliphatic amines. Towards ordinary reducing agents, ricinine exhibits considerable stability, but by hydrogen in presence of platinum black it is slowly converted into tetrahydricinine,  $C_8H_{12}O_2N_2$ , which is far less poisonous than ricinine and forms a readily soluble, crystalline *hydrochloride*,  $C_8H_{12}O_2N_2 \cdot HCl$ , m. p. 212—215°, a crystalline *platinichloride*,  $(C_8H_{12}O_2N_2)_2 \cdot H_2PtCl_6$ , decomposing at about 222—225°, and an *aurichloride*,  $C_8H_{12}O_2N_2 \cdot HAuCl_4$ , sparingly soluble in water. Tetrahydricinine gives precipitates with a large number of alkaloid reagents. Hydrogenation of ricininic acid yields methylamine.

When heated with concentrated hydrochloric acid at 145°, both ricinine and ricininic acid yield ammonia and the base,  $C_7H_9O_2N$  (compare Maquenne and Philippe, *loc. cit.*), which is also obtained by the action of 57.4% sulphuric acid on ricininic acid at 140°. Under the latter conditions, ricinine gives a base,  $C_7H_9O_2N$  ( $+3H_2O$ ), which crystallises in shining, felted needles, m. p. 55—57° or 112—114° (anhydrous), and yields a *platinichloride*,  $(C_7H_9O_2N)_2 \cdot H_2PtCl_6$ , m. p. 198—199°, an *aurichloride*,  $(C_7H_9O_2N)_2 \cdot HAuCl_4 \cdot H_2O$ ,

m. p. 129—131° (dried in a vacuum), and a *bromine* additive compound, m. p. 95° or 110° (dry); various reactions of this base, which exhibits normal cryoscopic behaviour in water, are described. The decomposition of ricinine by sulphuric acid is expressed by the equation  $C_8H_9O_2N_2 + 2H_2O = NH_3 + CO_2 + C_7H_9O_2N$ , and that of ricininic acid by  $C_8H_9O_2N_2 + 2H_2O = NH_3 + CO_2 + C_7H_9O_2N$ .

Both ricinine and the base,  $C_7H_9O_2N$ , contain one methoxy-group in the molecule; the former yields neither a benzoyl nor an acetyl compound, but with bromine it gives the *bromo*-derivative,  $C_7H_8O_2N_2Br$ , m. p. 226—230° (compare Evans, A., 1900, i. 309; *ibid.*, *loc. cit.*). Ricininic acid cannot be converted into ricinine by the ordinary methods of methylation.

Since, under certain experimental conditions, ricinine gives Feidel's and the murexide reactions, it is possible that its molecule contains a pyrimidine ring.

T. H. P.

**Vicine.** I. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 65, 258—264. Compare Levene, A., 1914, i. 1004).—The author's preparation had m. p. 239—242° (decomp.). A 10% solution in 10% sulphuric acid had  $[\alpha]_D^{25} = 8.77^\circ$ , whilst a 6.6% solution in *N*/5-sodium hydroxide gave  $[\alpha]_D^{25} = 12.1^\circ$ . On hydrolysis with *N*-sulphuric acid, it yielded 59.3% and 60.05% of a sugar.

identified definitely as dextrose. The elementary analysis corresponded with  $C_{10}H_{16}O_7N_4$ . J. C. D.

**Abnormal Behaviour of Glyoxalinecarboxylic Esters and Anilides towards Diazonium Salts.** ROBERT GEORGE FARGHER and FRANK LEE PYMAN (T., 1919, 115, 1015—1020).

**Partition of the Benzene Derivatives and the Benzene Carbon in the Protein Molecule.** E. and H. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1919, 105, 242—248).—An attempt to gain information as to the partition of the cyclic amino-acids in proteins by a study of their degradation products formed during putrefaction. From putrefied fibrin there were isolated 1.26% of indole, either in the free form or as indoleacetic acid, 2.85% of phenol, free or as hydroxy-acids, and 1.27% of  $\beta$ -phenylpropionic acid. A study of these quantities throws light on the amounts of tyrosine, tryptophan, and phenylalanine originally present in the fibrin, and it is suggested that such studies might be of value in determining the biological value of proteins. J. C. D.

**Preparation of Protein Free from Water-soluble Vitamine.** THOMAS B. OSBORNE, ALFRED J. WAKEMAN, and EDNA L. FERRY (*J. Biol. Chem.*, 1919, 39, 35—46).—The persistence with which the water-soluble vitamine is retained by edestin suggests that it is chemically combined therewith. Caseinogen, lactalbumin, gliadin, and orovitelin as prepared by the usual methods do not appear to carry this vitamine as an impurity. The water-soluble vitamine present in yeast is not entirely destroyed by digestion with 0.1N-sodium hydroxide for twenty-one and a-half hours, followed by heating on the water-bath for two hours. J. C. D.

**Effect of Various Acids on the Digestion of Proteins by Pepsin.** J. H. NORTHROP (*J. Gen. Physiol.*, 1919, 1, 607—612).—The rate of digestion of gelatin, egg-albumin, edestin, blood-albumin, and caseinogen by pepsin in the presence of hydrochloric, nitric, acetic, sulphuric, oxalic, phosphoric, and citric acids was followed by measuring the increase in free amino-groups by the method of Van Slyke (A., 1913, ii, 1084). The estimations were made at two ranges of hydrogen-ion concentration,  $p_H = 1.0$  to 1.5 and  $p_H = 2.5$  to 3.5. The rate of hydrolysis of all the proteins studied was found to be identical for all the acids except acetic acid. These experiments show that the physical properties of the solution, such as viscosity, have little or no effect on the rate of digestion. The simplest explanation of the results would seem to be that the rate of digestion of the protein is determined by the amount of acid protein salt formed. J. C. D.

**The Proteins of Fenugreek Seeds.** H. E. WUNSCHENDORFF (*J. Pharm. Chim.*, 1919, [vii], 20, 86—88).—Fenugreek seeds contain 27% of proteins; the latter consist of globulin, 25%; two albumins, 20%; and a nucleoprotein, 55%. The nucleoprotein is rich in iron (3.99%) and phosphorus (1.58%); on hydrolysis with

10% hydrochloric acid for two hours at 100°, it yields alanine 1.6%, leucine 2.50%, phenylalanine 2.5%, glutamic acid 35.71%, aspartic acid 1.32%, tyrosine 4.65%, arginine 3.15%, histidine 0.75%, proline 3.80%, glycine and lysine none. A solution of the substance in alkali hydroxide has  $[\alpha]_D -97.7^\circ$ . W. P. S.

**Salmine.** MATHILDE NELSON-GERHARDT (*Zeitsch. physiol. Chem.*, 1919, **105**, 265—282).—The author has found that there is an increase in acidity on hydrolysis of salmine similar to that observed by Goto in the hydrolysis of clupeine (A., 1903, i. 303). The cause of this increase is discussed. Sørensen's explanation ("Ergebnisse der Physiologie," 1912), based on the keto-enol tautomerism of the peptide linkings, demands that the original acidity returns when all these linkings are broken. This theory holds in the case of certain examples, such as glycine anhydride and leucylglycine. If it is to apply to the hydrolysis of salmine, it is necessary to assume that the process ceases before all the peptides are resolved. On investigation, peptides of the monoamino-acids were found to be present, and when the hydrolysis was completed by decomposition of these complexes, the acidity returned to the original value.

There is, however, evidence of another cause of increased acidity. Search for a new dibasic monoamino-acid was unsuccessful. Other possible causes are considered. J. C. D.

**Bacterial Catalase. III.** MARTIN JACOBY (*Biochem. Zeitsch.*, 1919, **95**, 124—130).—The preparation of a highly active catalase fraction from *Bacillus proteus* is described. J. C. D.

**Studies on Lipase.** GEN-ITSU KITA and MINORU OSUMI (*J. Tokyo Chem. Soc.*, 1918, **39**, 387—422).—On account of discrepancy among various workers on the question of relationship between acid and lipase, the authors conducted extensive studies on (1) the medium for the lipolytic enzyme, (2) optimum concentrations of the different acids for activation of the zymogen, (3) the effect of washing, and (4) the effect of alcohol, water, and various other substances. This paper is partly polemical with regard to Tanaka's paper (*ibid.*, **34**, 737). Castor beans are used for the source of lipase and soja-bean oil for the substratum. The results confirm Hoyer's work that the function of acid is solely to activate the zymogen, and the activated lipase can act without the addition of any acid, but after repeated washing a little addition of an acid will accelerate the reaction. Sensitivity of activated lipase against an acid depends entirely on the amount of the oil present in the medium. If activated lipase is left in an acid without any oil and then later the oil is added, no hydrolysis will take place, whereas if the oil and the enzyme are put together from the beginning, the hydrolysis will occur even to the extent of 80%. The optimum concentration of various acids for activation varies according to the kind of acid used, the stronger acids requiring fewer c.c. of normal solution than weaker acids, but the extent of hydro-

lysis is always greater with the weaker acid. Using 2.5 grams of the castor beans + 25 grams of the oil + 5 c.c. of water (including c.c. of the acid used), incubating at 39° for three hours, the amount of *N*-nitric acid necessary to give the maximal hydrolysis (32.9%) is 0.6 c.c.; for *N*-sulphuric acid, 0.75 c.c. The maximal digestion being 37%; for *N*-oxalic acid, 0.75 c.c., giving 36.8%; 0.75 c.c. of *N*-tartaric acid gives 41.8%; 1 c.c. *N*-lactic acid, 41.5%; 1.5 c.c. *N*-citric acid, 56.2%; 4 c.c. of *N*-succinic acid, 45.97%; and 3 c.c. of *N*-acetic acid, 54.4%. In making a permanent lipase preparation, the optimum amount of acids should be added according to (1) the amount of the oil the seed contains, the greater the amount of the oil the smaller the number needed; (2) the size of the crushed beans, the smaller the granules the less the amount of the acid needed; (3) temperature, the higher the less amount of acid; and (4) time, the longer the treatment the less the acid necessary. Dilution of the acid, maintaining in the medium the absolute amount of the acid necessary for the maximal amount of hydrolysis, lessens the lipolytic power, especially in the case of strong acids. The strong acids once used for activation of zymogen will have no effect for activating a new bean, but the weak acids will. When the castor bean is washed with water containing sodium or calcium chloride, its enzymic power is reduced, probably by loss of globulin. Addition of acetic acid will counteract this salt effect. Unlike other enzymes, lipase is exceedingly sensitive to alcohol, but ether, benzene, and carbon disulphide will not destroy it. Lipase in aqueous solution loses its activity very quickly if no oil is present.

CHEMICAL ABSTRACTS.

**Manufacture of the Organic Phosphorus Reserve Compound of Green Plants, and Salts Thereof.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat., 130456).—A pure sodium salt of the organic phosphorus reserve compound is prepared from the impure material through the intermediate precipitation of the ferric salt, its decomposition by sodium hydroxide, and the addition of alcohol to the filtered solution. The crystalline mass which separates gives on recrystallisation from water efflorescent prisms of the composition  $C_6H_8O_{24}P_4Na_{12} \cdot 47H_2O$ , m. p. 49°. The anhydrous salt is a stable, white, non-hygroscopic powder, alkaline in reaction and insoluble in organic solvents. Pure alkaline earth, lead, and copper salts are obtained by double decomposition, and from them the pure acid of the phosphorus compound is prepared by the action of oxalic acid or hydrogen sulphide, as the case may be. [See, further, *J. Soc. Chem. Ind.*, 1919, 739A.] G. F. M.

**Cytidine-Phosphoric Acid.** P. A. LEVENE (*J. Biol. Chem.*, 1919, 39, 77—81. Compare A., 1918, i, 138).—The preparation of the pure brucine salt of cytidine-phosphoric acid is described. From this may be prepared the barium salt,  $C_9H_{12}O_8N_3P_3Ba$ . The optical rotation of the air-dried substance was  $[\alpha]_D^{25} + 14.0^\circ$ . By hydrolysis of the barium salt by heating with 10% sulphuric acid

in a sealed tube at 125°, cytidine was formed, where cytosine had been expected. No explanation of this result is given. No uridine was found in the mother liquors from the cytidine picrate.

J. C. D.

**Sodium Inositol-hexaphosphate (a Correction).** S. POSTERNAK (*Compt. rend.*, 1919, 169, 337—338. Compare this vol., i, 426).—A stable form of this compound containing only 35 mols. H<sub>2</sub>O is slowly deposited from concentrated solution at about 20°. It melts at 58—59° and loses water of crystallisation at 120°, and the crystallographic measurements recently given (this vol., i, 426, 433) refer to this substance and not to the efflorescent hydrate containing 44 mols. H<sub>2</sub>O.

G. F. M.

**Substituted Phenylarsinic Acids and their Reduction Products, and the Estimation of Arsenic in such Compounds.** ROBERT GEORGE FARGHER (*T.*, 1919, 115, 982—992).

**Formaldehyde Derivative of Arsenophenylglycine.** K. J. OECHSLIN (U.S. Pat. 1299214).—Arsenophenylglycine is dissolved in a 6% solution of sodium carbonate and treated with formaldehyde. On the addition of alcohol or acetone to the solution, a sodium salt of the reaction product is obtained, which possesses a light yellow colour, and may be dried and kept in the air for some time without decomposition.

CHEMICAL ABSTRACTS.

**Acetylarsenophenylglycine.** K. J. OECHSLIN (U.S. Pat. 1299215).—A solution of acetylphenylglycinearsinic acid (50 grams) and sodium hyposulphite (500 grams) in water (2500 c.c.) is heated for two hours at 45—55°, and acetic acid (70 c.c.) is then added. Acetylarsenophenylglycine is precipitated in light yellow flakes. Acetylarsenophenylglycine also may be prepared by dissolving arsenophenylglycine in sodium carbonate solution and successively adding acetic anhydride and hydrochloric acid.

CHEMICAL ABSTRACTS.

## Physiological Chemistry.

**Absorption of Light by Neutral Solutions of Oxyhæmoglobin.** PAUL HÄM (*Biochem. Zeitsch.*, 1919, 95, 257—265).—The absorption of light by neutral solutions of blood or of oxyhæmoglobin is very little different from that of solutions in aqueous sodium carbonate. The difference is attributed to the presence of small amounts of methæmoglobin.

J. C. D.

**Behaviour of Inulin in the Animal Body. II. Inulin in the Alimentary Canal.** RUTH OKEY (*J. Biol. Chem.*, 1919, 39, 149—162).—Inulin is hydrolysed in vitro by hydrochloric acid of a concentration approximately the same as that in the normal gastric juice provided a sufficiently long period of hydrolysis is allowed. During the time normally occupied by food in the stomach, the amount of hydrolysis is comparatively small. The presence of an enzyme capable of producing a reducing sugar from inulin has been demonstrated in sterile extracts of three samples of human faeces from radically different types of diet. Negative results were obtained with samples from a dog and guinea-pigs.

J. C. D.

**Genesis of Thiocyanic Acid in Animals. VII. From what Substances is Normal Thiocyanic Acid Derived in Animals?** SERAFINO DEZANI (*Arch. Farm. speriment. sci. aff.*, 1918, 26, 257—273; from *Chem. Zentr.*, 1919, iii, 65. Compare this vol., i, 423).—The negative results obtained with amino-acids and derivatives of purine in the case of the dog are in contrast with the positive results of Willanen (A., 1906, ii, 784) in the case of the rabbit. The latter experiments have been repeated, particular attention being given to the influence of the nourishment. No increase in thiocyanic acid could be detected after administration of glycine, asparagine, guanine, or creatinine; evidence in favour of the hypotheses of Nencki and of Bruylants is therefore not obtained.

H. W.

**Quinine and Hydroquinine in the Human Body. Behaviour of Quinine towards Red Blood Cells.** J. HALBERKANN (*Biochem. Zeitsch.*, 1919, 95, 24—45).—The fate of these two substances in the body is discussed. It is shown that quinine may be taken up and retained by the erythrocytes.

J. C. D.

**Presence of Histamine ( $\beta$ -Iminazolyethylamine) in the Hypophysis Cerebri and Other Tissues of the Body and its Occurrence Among the Hydrolytic Decomposition Products of Proteins.** JOHN J. ABEL and SEIKO KUBOTA (*J. Pharm. Expt. Ther.*, 1919, 13, 243—300).—The experimental findings support the view previously expressed (*Proc. Nat. Acad. Sci.*, 1917, 3, 507—517) that the oxytoxic principle of the hypophysis is not a hormone or substance specific to this organ, but is a rather widely distributed substance, everywhere the same, which may have its origin in the various tissues or in the gastric or intestinal mucosa, or may be absorbed as such from among the products of digestion. This substance is now believed to be histamine, a substance which stimulates plain muscle in minute doses and which depresses the circulation and causes a shock-like prostration when administered in doses which lie beyond the limit of toleration. The base was isolated with certainty from pituitary tissue and gastric and intestinal mucosa of the dog, and its presence in liver tissue and striated muscle was detected. The amine was also found in erepton (com-

pletely digested meat), Witte's peptone, and amongst the products of hydrolysis of pure proteins with hydrochloric acid. It is suggested that histamine plays an important rôle as a stimulant for the gastric and intestinal musculature and as a dilator of capillaries during digestion. J. C. D.

**[Physiological Action of] Optical Isomerides. V. The Tropeines.** A. R. CUSHNY (*J. Pharm. Expt. Ther.*, 1919, 13, 71—93. Compare A., 1909, ii, 420).—Atropine is twenty times as strong as *d*-hyoscyamine in affecting the terminations of the chorda tympani in the dog. Therefore *l*-hyoscyamine would have an action forty times as great as that of its optical isomeride. The difference between the effects of atropine and *d*-hyoscyamine on cardiac inhibition is of the same order as on salivary secretion. The physiological action of a number of tropeines has been examined. Tropeine itself is devoid of typical atropine action, but many tropeines, especially those which contain a benzene nucleus, show the characteristic effects. This is particularly intensified where there is a hydroxyl group or an asymmetric carbon atom in the side-chain. The most powerful action is shown by members of this type which contain an acid of the benzene series, together with a hydroxyl group and asymmetric carbon atom in the side-chain, and the whole molecule of which is laevorotatory. J. C. D.

**Vitamine Studies. IV. Antineuritic Properties of Certain Physiological Stimulants.** R. ADAMS DUTCHER (*J. Biol. Chem.*, 1919, 39, 63—68).—Thyroxin (the active principle of the thyroid), desiccated thyroid, pilocarpine, and tethelin apparently produced definite relief in certain acute cases of avian polyneuritis. The response was not, however, of the type obtained when vitamine preparations were given. J. C. D.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Biochemistry of *Bacillus Acetoethylicum* with Reference to the Formation of Acetone.** JOHN H. NORTHROP, LAUREN H. ASHE, and JAMES K. SENIOR (*J. Biol. Chem.*, 1919, 39, 1—21).—The description of an organism termed *Bacillus acetoethylicum* which was isolated from old potatoes is given. The organism resembles in some ways the *B. macerans* described by Schardinger (*Centr. Bakt. Par.*, 1905, ii, 14, 772), but it is not thought that the two are identical. This organism produces acetone and ethyl alcohol from starch or sugar. The optimum conditions for the fermentation have been studied, and a semi-continuous method for carrying on the process is described. [See, further, *J. Soc. Chem. Ind.*, 1919, October.] J. C. D.



**Formation of Acids by Moulds and Yeast. III.** FRIEDRICH BOAS and HANS LEBERLE (*Biochem. Zeitsch.*, 1919, **95**, 170—178. Compare *ibid.*, 1918, **90**, 78; **92**, 171).—When both ammonium sulphate and acetamide are present as sources of nitrogen for *Aspergillus niger* growing in an artificial culture solution, only the ammonium sulphate is utilised, notwithstanding that acetamide would from some point of view appear a more suitable material for protein synthesis, particularly as its utilisation does not necessitate the liberation of a toxic substance, such as the sulphuric acid liberated in the utilisation of ammonium sulphate. From similar tests with glycine and acetamide, it would appear the glycine is utilised, whereas the amide is almost untouched. Experiments in which the mould has a choice between ammonium sulphate and peptone show that preferential utilisation of the former source of nitrogen occurs. In fact, when *A. niger* is given the choice between two sources of nitrogen, one of which is an ammonium salt and a strong mineral acid, it utilises the ammonium salt alone, in spite of the fact that this leads to a rise of hydrogen-ion concentration with all its deleterious consequences.

Apparently the degree of dissociation of the ammonium salt is an important factor. J. C. D.

**The Formation of Soluble Starch in Relationship to Selective Nitrogen Metabolism.** FRIEDRICH BOAS (*Ber. Deut. bot. Ges.*, 1919, **37**, 50—56).—It has been previously shown that soluble starch is formed from many carbohydrates by *Aspergillus niger* when the hydrogen-ion concentration has attained a certain value. The author has based a method of studying selective nitrogen metabolism on this observation; thus, for instance, when in a sugar solution ammonium chloride is consumed in addition to amino-acids, the hydrogen-ion concentration rapidly increases in consequence of the liberation of the greatly dissociated hydrochloric acid, so that favourable conditions are developed for the formation of soluble starch, which can readily be detected by the iodine test. The following groups have been studied: mixtures of ammonium salts (ammonium chloride and ammonium phosphate or citrate); amino-acids and peptones in the presence of ammonium chloride; acid amides (carbamide) and ammonium chloride. The latter differs from all the other sources of nitrogen which were investigated in that it is strongly dissociated. Experiments show that in mixtures of nitrogenous substances with varying degrees of dissociation, the magnitude of the latter determines the absorption into the cell. In comparison, the solubility of the substance in lipoids has but little influence. The more strongly dissociated source of nitrogen is invariably utilised even when powerfully poisonous products are thereby developed, and when other non-poisonous, lipid-soluble and suitable sources of nitrogen are present. Absorption is not regulated by the mould, but occurs exclusively according to physico-chemical properties. From the biological point of view, the mould invariably utilises the worse source of nitrogen. H. W.

**Parallel Formation of Carbon Dioxide, Ammonia, and Nitrate in Soil.** P. L. GAINES (*Soil Sci.*, 1919, 7, 293—311).—

In laboratory experiments, purified air was drawn in a downward direction through a column of loam soil supported in a cylinder, and then through glass beads moistened with a solution of sodium hydroxide, and afterwards through glass beads moistened with dilute acid. Usually, six of these apparatus were connected in series. Estimations of the carbon dioxide and ammonia retained by the absorption vessels determined the amounts of these gases given off, and after each experiment the top layer of soil was removed and examined for ammonia and nitrates. The carbon dioxide in the soil was not taken into consideration. One per cent. of cotton-seed meal was added to the soil as a substance readily decomposed by bacteria. Observations on variation in the moisture content of the soil showed that this factor had little effect on the carbon dioxide evolved provided the amount of water was above a minimum of 12 c.c. per 100 grams of soil. The maximum amount of carbon dioxide was produced during the second day. The production of ammonia ran parallel with that of carbon dioxide, except that the optimum minimum of moisture was rather higher. The accumulation of nitrates did not begin until the fifth day, and the amount increased regularly with a corresponding diminution in that of the ammonia. Variations in air supply had a marked effect on bacterial activity. Unless the current of air was continuous, there was a distinct diminution and delay in the changes produced. In the case of ammonia, there was a permanent diminution in amount; in the other two cases, the amount of carbon dioxide finally reached that produced in continuous aeration, whilst the amount of nitrate became inversely proportional to aeration. Experiments were made also with 1% of dried blood added to the soil. With this substance, the production of carbon dioxide was much diminished and that of ammonia relatively increased, probably due to the higher nitrogen content of the blood over the cotton-seed meal and to the amount of readily oxidisable carbon being insufficient to supply energy for complete decomposition.

J. H. J.

**Action of Capillary-active Substances on Plant Seeds.**

I. TRAUBE and HEDWIG ROSENSTEIN (*Biochem. Zeitsch.*, 1919, 95, 85—100. Compare Traube and Marusawa, A., 1916, i, 106).—The influence of a large number of substances on the germination and growth of seeds has been investigated. Narcotics, such as chloroform, ether, and urethane, produce a narcotic action which is in certain respects similar to the effect on the animal organism. Many substances, such as toluene, chlorobenzene, piperidine, pyridine, aniline, acetone, isobutyl acetate, and isoamyl alcohol are strongly toxic. Naphthalene and thymol vapour may hasten germination if the exposure is not too long, whilst *m*-cresol may in certain concentrations beneficially influence the growth of barley.

The higher fatty acids exert a marked stimulating action on the

rate of germination, whereas the lower fatty acids in low concentrations are very poisonous.

J. C. D.

**The Opposed Action, Antagonism, of Manganese and Iron on the Growth of Wheat.** W. E. TOTTINGHAM and A. J. BECK (*Plant World*, 19, 359—370; from *Chem. Zentr.*, 1919, iii, 110).—Small quantities of manganese chloride are harmful to the root system and inhibit the positive action of ferric chloride. Both salts are poisonous at greater concentrations, at which the ferric chloride restricts the action of manganese chloride. Small quantities of manganese chloride induce more rapid growth of the plant, but the same antagonism is observed as with the root system. In the presence of sodium hydrogen carbonate, manganese chloride is disadvantageous to the roots and green parts even in small amounts, and distinctly poisonous at higher concentrations. Contrary to previous observations, ferric chloride encourages the growth of terminal shoots, probably on account of the alkaline nature of the nutrient solution.

H. W.

**The Alkaloids in Plant Injury.** O. TUNMANN (*Biochem. Zeitsch.*, 1919, 95, 164—169).—No accumulation of alkaloid was found to follow injury to the leaves of *Atropa belladonna*, L., or *Pilocarpus pennatifolius*, Lem., whether caused by animals or by artificial methods. This is not in agreement with the work of Troegele (*Diss.*, Würzburg, 1900).

J. C. D.

**Nutritive Factors in Plant Tissues. II. The Distribution of the Water-soluble Vitamine.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1919, 39, 29—34).—The water-soluble vitamine is present in the bulb of the onion, the root of the turnip, the leaves, stem, and roots of the beet, and the fruit of the tomato. A comparison of mature and immature plants of clover, lucerne, and timothy grass indicates that the immature plants are the richer sources of water-soluble B. The bearing of this observation on the food value of hay is discussed.

J. C. D.

**Relation of Sulphates to Plant Growth and Composition.** H. G. MILLER (*J. Agric. Res.*, 1919, 17, 87—102).—Pot experiments were made with three soils, one selected for its high content of sulphur, namely, 0.183%, one because it had responded to free sulphur treatment, and one because it did not respond to any sulphur treatment. The plants grown were red clover, oats, and rape. The fertilisers used were calcium and sodium sulphates and free sulphur. The last was added with calcium carbonate to the soil at the time of sowing the seed; the other two were added daily in the form of 0.02% solutions. A solution of sodium nitrate was added daily in order to provide excess of nitrogen in every case. A similar set of experiments was made in which the soil was replaced by washed sand, to which was added a sterilised extract of the soil. The weight of the crops was noted, and the content of sulphur and

nitrogen estimated. It was found in every case that enhanced growth took place as compared with the control tests, especially marked in the case of the oats and clover. As this enhanced growth took place in the sand as well as in the soil, it is concluded that the sulphates and free sulphur acted directly in the promotion of growth. In the case of clover, there was a marked increase in the nitrogen content of those plants grown in soil over those grown in sand, doubtless due to stimulation of the legume bacteria by the fertilisers added, as was evidenced by the increased root development and number of nodules in these cases.

J. H. J.

### Nitrogen and Other Compounds in Rain and Snow.

JACOB E. TRIESCHMANN (*Chem. News*, 1919, 119, 49).—A summary of the analyses of forty-six samples of rain and snow collected at Cornell between October 1st, 1918, and June 15th, 1919, is given. The total precipitation corresponds with 56.3 cm. of rain, and contained 572 kilos. of chlorine (944 kilos. of sodium chloride), 1.679 kilos. of sulphates as  $\text{SO}_3$ , and 5.853 kilos. of nitrates per hectare. The phosphates only amounted to 0.0089 kilos. per hectare. Only fifteen samples contained sufficient sulphate for analysis, and eleven other samples showed the merest trace of sulphate. The highest sulphate content was 0.262 part per million, the average for the period being 0.03 part per million. Five samples showed a trace of phosphate, but only four contained sufficient for estimation. The highest content of phosphate was 0.03 part per million, the average being 0.002 part per million. The chlorine content averages 11.12 parts per million, and varies between 6.10 and 25.70 parts per million. The average of the total nitrogen was 1.046 parts per million. The free ammonia is represented by 0.407, albuminoid ammonia 0.366, nitrate 0.255, and nitrite 0.018 part per million. The total nitrogen is fairly constant, and forty-three of the forty-six determinations lie between 0.18–0.45 kilos. of nitrogen per hectare. The amount of nitrogen increased from 0.669 part per million to 1.134 parts per million from February to June, that is, an increased amount of nitrogen is supplied to the soil during the growing period.

J. F. S.

### Ammonia-fixing Capacity of Calcium Sulphate.

FIRMAN E. BEAR and ALBERT C. WORKMAN (*Soil Sci.*, 1919, 7, 283–291).—It has been observed that the addition of calcium sulphate to manure tends to prevent loss of ammonia. To test the nature of this reaction under simple conditions, laboratory experiments were carried out in which the manure was replaced by paper pulp, which was mixed with calcium sulphate and placed in a bottle. A solution of ammonium carbonate was poured over the pulp, giving a water content of 75%. The bottle was kept at different temperatures from 20° to 80°. A current of air freed from ammonia and carbon dioxide was drawn through the mixture in the bottle, and then through absorption vessels containing standard

acid. Observations were continued over ninety-five days, air being drawn through about daily for ten minutes at a time. The nitrogen loss without calcium sulphate was 5.6225 grams, and with calcium sulphate 1.1419 grams. More nitrogen was lost at the higher temperatures, and the proportion held back by the calcium sulphate was less at those temperatures. Under the conditions of the experiment, the chemical reaction was probably that of a simple double decomposition. [See also *J. Soc. Chem. Ind.*, 1919, 731A.]

J. H. J.

**Electrical Conductivity as a Measure of the Content of Electrolytes of Vegetable Saps.** DOROTHY HAYNES (*Biochem. J.*, 1919, 13, 111—123).—The causes of the low values obtained in conductivity measurements in fruit juices containing considerable quantities of organic acids are submitted to examination. These low figures are due to two principal causes, first, the action of non-electrolyte (compare Arrhenius, A., 1892, 1038), and secondly, the mutual action of salts and acids in repressing dissociation. The conclusions of Dixon and Atkins (A., 1913, i, 1422) drawn from a comparison between the juice from plant organs when pressed without previous treatment and the juice of the same organs when treated by exposure to liquid air before pressing are criticised. It is suggested that there is very little evidence for the marked differences which they assume to exist in the proportional composition of the two kinds of sap. It is further suggested that these experiments afford no evidence that the protoplasm of the cells of tissue under pressure is permeable to electrolytes to any considerable extent. A formula is advanced by means of which, in certain cases, conductivity measurements may be reduced to standard conditions.

J. C. D.

**Examination of the Bark of Croton gubouga. Isolation of 4-Hydroxyhygric Acid.** JOHN AUGUSTUS GOODSON and HUBERT WILLIAM BENTLEY CLEWER (*T.*, 1919, 115, 923—933).

**Action of Fluorides on Vegetation. B. Field Trials.** ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1919, 169, 115—122).—As the result of field trials, using amorphous calcium fluoride as the source of fluorine, the authors find that this element increases the crop yield in certain species of plants. The calcium fluoride was applied at the rate of 55.8 grams per sq. metre to a poor, sandy soil. Increased crop yields varying from 5.2 to 58.7% were obtained with wheat, oats, carrots, potatoes, peas, beans, and poppies, whilst beet, kidney beans, and cabbage gave either no increase or a decrease. In the case of potatoes, there was no marked increase in the yield in the year of application of the calcium fluoride, but a very decided increase (58.7%) in the next year. Most of the other crops showed little, if any, residual effect in the second year.

W. G.

## General and Physical Chemistry.

**Index of Refraction and Molecular Refraction of Aqueous Solutions of Nicotine.** AUGUSTO LEVI (*Atti R. Ist. Veneto Sci.*, 1915, 75, 465—479).—Measurements were made by the method of minimum deviation on a good spectrometer. The temperature was not constant, but was kept sufficiently near 24°. Sixteen concentrations were used. Pufrich's method of calculation is:  $P[(n-1)/d][(1-\alpha C)/(1-C)] = P_1[(n_1-1)/d_1] + P_2[(n_2-1)/d_2]$ .  $P$ ,  $P_1$ ,  $P_2$  are the weights,  $n$ ,  $n_1$ ,  $n_2$  the refractive indices, and  $d$ ,  $d_1$ ,  $d_2$  the densities, respectively, of the mixture and of the two components.  $C$  is the coefficient of contraction, and equals  $(d-d_0)/d$ , in which  $d_0$  is the density the mixture would have if no contraction took place on mixing, and  $\alpha$  is a constant derived from the empirical relation  $(d-d_0)/d = \alpha[(n-1) - (n-1)_0]/(n-1)$ , in which  $(n-1)_0$  is the value  $n-1$  would have if no contraction took place. This gave results more consistent with experimental data, and indicated that methods of calculation based on the hypothesis that the  $n$  of mixtures is additive are not accurate. The molecular fraction for water ( $q_a$ ) and nicotine ( $q_b$ ) was calculated by the method of Schulze.  $q_a + q_b = 1$ ;  $q_a = (p_a/m_a)/[(p_a/m_a) + (1-p_a)/m_b]$ ;  $q_b = (1-p_a/m_b)/[(p_a/m_a) + (1-p_a)/m_b]$ ; the experimental molecular refraction calculated from the rule of mixtures, according to the Dolezalek-Schulze theory, shows that the water and nicotine form solutions without dissociation phenomena.

## CHEMICAL ABSTRACTS.

**Optical Activity. I. Temperature-rotation. Curves for the Tartrates at Low Temperatures.** T. S. PATTERSON and K. L. MOUDGILL (*Proc. Roy. Soc. Edin.*, 1919, 39, 18—34).—Rotation-temperature curves have been produced from measurements of the rotation of ethyl *d*-tartrate and isobutyl dibenzoyl-*d*-tartrate dissolved in cinnamaldehyde and ethylene dibromide respectively at a series of temperatures from 0—181° in the first-named solvent and 17.7° and 39.7° in the last-named solvent. A consideration of the present results and previously published results T., 1908, 93, 1844; 1912, 101, 378; 1913, 103, 152; 1916, 109, 1145) shows that a general temperature-rotation curve may be produced for all tartrates.

J. F. S.

**Value of the Silver Oun.** W. M. HICKS (*Phil. Mag.*, 1919, vi, 38, 301—317. Compare A., 1913, ii, 810).—A theoretical paper in which an attempt is made to calculate the value of the un for silver to an accuracy of 1 per 100,000. In general, it is shown that  $q = 361.7837 + 0.001628d.N \pm 0.0038$ , for silver  $\delta = 21.0470 + 0.001894d.N \pm 0.0045$ . If the atomic weights in terms of the silver value are determined from the un, the values are independent of the actual  $N$  used, provided it can be taken as the same for all elements. They should be calculated, therefore, either

with  $N=109675$  if in *R.A.* or  $109678.6$  if in *I.A.* and the value  $q=361.7837\pm0.0038$  used.

J. F. S.

**Series Spectra according to the Bohr Atom Model.** FRANZ TANK (*Ann. Physik*, 1919, [iv], 59, 293—331).—A mathematical paper in which relationships of the series spectra are deduced on the basis of Bohr's conception of the atom. These relationships are examined in connexion with the series spectra of hydrogen, helium, parhelium, and lithium.

J. F. S.

**Principle of Choice and the Displacement Law for Series Spectra.** W. KOSSEL and A. SOMMERFELD (*Ber. Deut. physikal. Ges.*, 1919, 21, 240—259).—A theoretical paper in which the co-ordination of spectrum lines into series on the basis of the quantum theory is discussed. It is shown that the series of doublets of the alkaline earths are spark spectra; their character as a system of doublets explains itself from the doublet character of the arc spectrum of the alkalis. A simple numerical relationship exists between the spark spectrum of the alkaline earths and the arc spectrum of the next preceding alkali metal.

J. F. S.

**Effect of an Electric Field on the Pressure Displacement and the Broadening of Series Lines.** M. RITTER (*Ann. Physik*, 1919, [iv], 59, 170—184).—The effect of an electric field of approximately 26,000 volt/cm. on the series lines of zinc, mercury, lithium, and calcium is to cause the pressure displacement and the unsymmetrical broadening to increase along a series with increasing member number, and also with decreasing wave-length. The sign of the displacement by an electric field is always the same as the sign of the displacement by increase of pressure and the sign of the dissymmetry. These results confirm experimentally Stark's hypothesis that the pressure displacement and the unsymmetrical broadening is brought about by an intra-molecular electric field.

J. F. S.

**Structure of the Band Spectra of Burning Hydrocarbons.** T. HEURLINGER and E. HULTHÉN (*Zeitsch. wiss. Photochem.*, 1919, 18, 241—248).—The band spectrum of an acetylene flame has been photographed in the first three orders by means of a concave grating 6.4 m. diameter ruled 400 lines per cm. The bands in general can be represented by three whole numbers,  $m$ ,  $n$ ,  $p$ , and a second class of bands in which the  $n$ ,  $p$ , values correspond with a system of six series,  $P_i$ ,  $Q_i$ , and  $R_i$  ( $i=1, 2$ ). The lines of these six series are given in the paper and the relationships between them worked out.

J. F. S.

**Effect of an Electric Field on the Spectrum Lines of Argon.** TOSHIO TAKAMINE and NOBORU KORUBU (*Mem. Coll. Sci. Kyoto*, 1919, 3, 281—285).—The Stark effect on the argon spectrum lines has been examined, using a field of 170,000 volt/cm., by Lo Surdo's method. The lines  $\lambda\lambda$  4933.5, 4510.9, 4335.4, 4333.7, 4300.2, 4272.3, 4259.5, 4200.8, 4198.4, 4191.0, 4182.0, 4164.4, 4158.7, 4153.0, 4132.0, 4046.0 Å. are all slightly displaced toward the red.

Practically all the lines affected by an electric field belong to the red spectrum of argon, and the so-called arc lines seem to be more easily affected than the spark lines. This is in keeping with the results obtained in the case of helium, calcium, and magnesium. The mercury line  $\lambda$  4339 Å. was found to be displaced about 0.7 Å. for the  $p$ -component and 0.5 Å. for the  $s$ -component toward the red end in a field of 53,000 volt/cm.

J. F. S.

**Effect of an Electric Field on the Spectrum Lines of Helium. III.** TOSHIO TAKAMINE and NOBORU KOKUBU (*Mem. Coll. Sci. Kyoto*, 1919, 3, 275—280. Compare A., 1918, ii, 253).—The effect of an electric field on the spectrum lines of helium has been continued with the lines  $\lambda\lambda$  4009, 3889, 3868, 3830, 3448, 3188, and 2945 Å.; these lines are examined for the first time. The lines  $\lambda\lambda$  4438, 4121, and 3965 Å., which have previously been stated to be slightly displaced by an electric field, are found to be resolved into a number of components all of which are displaced in the same direction. A striking similarity is noted between the Stark effect on the helium lines  $\lambda\lambda$  4388 and 4026 Å. and the H $\gamma$  line in the fact that the central line in the  $s$ -component is the strongest of all the components, and it is displaced toward the red as the field strength is increased. In the present work an echelon grating was used for examining the Stark effect, and the advantages of this arrangement are discussed. The faint line accompanying  $\lambda$  5876 and 4472 Å. has been examined in this way. Numerous diagrams and photographs are appended to the paper.

J. F. S.

**Effect of an Electric Field on the Spectrum Lines of Hydrogen. II.** TOSHIO TAKAMINE and NOBORU KOKUBU (*Mem. Coll. Sci. Kyoto*, 1919, 3, 271—273. Compare A., 1917, ii, 401).—Experiments previously described have been repeated with slight modifications; a tantalum cathode was used instead of an aluminum one, and the pressure in the tube was further reduced, so that it was possible to obtain a field strength of 150,000 volt/cm. It is shown that the central line in the perpendicular component of H $\beta$  is shifted about +1 Å. at a field of 130,000 volts/cm. In the case of the H $\beta$  line six  $p$ -components and three  $s$ -components were observed, a fact in keeping with the later work of Stark (*Ann. Phys.*, 1915, 48, 183). In the secondary hydrogen spectrum the authors have noted a further eleven lines in the region below  $\lambda$  4000 Å. which are affected by an electric field.

J. F. S.

**Spectrum Lines of Oxygen and Nitrogen in an Intense Electric Field.** USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1919, 3, 287—297).—The Stark effect on the spectrum lines of oxygen and nitrogen has been examined in fields up to  $16.5 \times 10^4$  volt/cm. and a positive result observed with the lines  $\lambda\lambda$  4100 and 4110 Å. of nitrogen and with some of the lines belonging to the first and second subordinate triplet series of oxygen. Excepting a few ambiguous cases, the amount of displacement or of separation of each of these lines is nearly equal respectively in both the parallel and



perpendicular components. The behaviour of the lines of the second subordinate triplet series of oxygen in the electric field is similar to that of the lines belonging to the second subordinate series of helium and parhelium. The effect on the spectrum lines of the first subordinate triplet series of oxygen is larger than that on the second subordinate triplet series. Each of the lines  $\lambda\lambda$  5329.5 and 4968.5 Å. of the first subordinate triplet series has two isolated components respectively in its immediate violet side. The isolation of the said components becomes smaller as the term number of the series increases. This is exactly similar to that of the isolated components of helium and parhelium. Diagrams and photographs of the resolved lines are appended to the paper.

J. F. S.

**Lithium Spectrum in an Electric Field.** USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 161—171).—The effect of an electric field of 30,000 volt/cm. on the lithium lines  $\lambda\lambda$  6103.8, 4602.4, 4132.4, and 4148.2 has been determined by Lo Surdo's method. The line  $\lambda$  6103.8 is unaffected by the field employed. In the case of the line  $\lambda$  4602 two vertical and two parallel components only were observed; the central component observed by Stark did not appear. The separation of the parallel components is somewhat greater than that of the perpendicular components. The intensity of the violet component is less than that of the red component. The line  $\lambda$  4132 is separated into three components, the displacement of the parallel components being somewhat smaller than those of the perpendicular components. The helium lines have been compared with the lithium lines under the same conditions of treatment. The peculiarity of the lines  $\lambda\lambda$  4602 and 4148.2 in the arc has been explained as due to the effect of an electric field on these lines. Photographs of the separated lines are appended to the paper.

J. F. S.

**Effect of an Electric Field on the Spectrum Lines of Calcium and Magnesium.** TOSHIO TAKAMINE and NOBORU KOKUBU (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 173—181).—Making use of Lo Surdo's method, the effect of an electric field on the calcium and magnesium lines has been investigated. Quantitative measurements have been made with the calcium lines  $\lambda\lambda$  4685, 4355, 4099, 4095, 4093, 3645, and 3631 Å. and with the magnesium lines  $\lambda\lambda$  4352, 3097, and 3093 Å. The maximum electric field employed was 90,000 volt/cm. The above-mentioned lines and others between  $\lambda\lambda$  5042 and 3624 Å. which were not measured were all displaced in one direction or the other in the electric field. In general, the lines belonging to the same series were affected in nearly the same way, and, further, each line constituting a triplet was affected in the same way. The latter is well shown in the case of the lines  $\lambda\lambda$  4099, 4095, and 4093 Å. belonging to the narrow triplet series. The magnesium triplet  $\lambda\lambda$  3838, 3833, and 3830 Å. seems to be an exceptional case, but as the lines are only very slightly affected, further experiments, using a larger dispersion, are

needed for confirmation. Photographs of the displaced lines are appended to the paper.

J. F. S.

**The Arc Spectrum of Dysprosium.** JOSEF MARIA EDER (*Sitzungsber. K. Akad. Wiss. Wien*, 1918, II A, 127, 1100—1228; from *Chem. Zentr.*, 1919, i, 914. Compare A., 1918, ii, 181).—It appears possible on spectroscopic evidence that an unknown element, closely related to terbium, is present in the terbium-dysprosium fractions, the spectrum of which is mixed with that of the actual terbium and dysprosium. To obtain further insight into this probability, the author has examined the arc spectrum of pure dysprosium over its whole length. The specimen used was supplied by Auer von Welsbach. The sulphate was converted into the chloride since the latter salts of the rare earths give more powerful arc spectra with less prominence of carbon bands than do the oxides or sulphates. The colour of the arc flame was pale green, but not nearly so intense as with cassiopeium and aldebaranum. The wave-length table given by the author contains 4385 lines, including many new ones in the red, yellow, and extreme ultra-violet regions. No definite evidence of fission of dysprosium is obtained, so that it may be regarded as a well-defined element which can be isolated in the pure condition by various processes of separation, and through the spectrum of which further information may be obtained with respect to the yet uncertain terbium. The lines of the dysprosium arc spectrum are generally sharp, and only broaden slightly after protracted illumination; in addition, a more or less well-defined band spectrum is shown in the visible portion. The first of these bands has its main edge at 5693 Å.U. The second, broadened band has its brightest edge at 5404; the main edge of the third, well-defined band lies at 5263. Contrary to the views of Eberhard, the lines of dysprosium are not generally present in the spectrum of the sun, in which the presence of this element cannot be detected.

H. W.

**Is the Absorption [of Light] (Vierordt) a Characteristic Value, Independent of the Apparatus (Spectrophotometer) Employed?** PAUL HÄRI (*Biochem. Zeitsch.*, 1919, 95, 266—271).

—The values are characteristic, and are not influenced by the type of apparatus, provided the construction and calibration of the instrument are satisfactory.

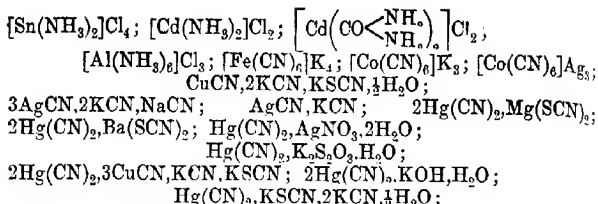
J. C. D.

**Absorption Spectra of Aqueous Solutions of Colourless Metallic Complex Salts.** YUJI SHIBATA, KURAZO FUKAGAWA, and ICH ASADO (*J. Tokyo Chem. Soc.*, 1919, 40, 311—333).—The following solutions were used:

$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ ;  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ ;  $\text{Ag}_2(\text{NH}_3)_2\text{SO}_4$ ;  $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$ ;  $[\text{Cu}(\text{CS} \leftarrow \text{NH}_2)_3]\text{Cl}$ ;

$[\text{Zn}(\text{NH}_3)_4]\text{Cl}_2$ ;  $\text{Zn}(\text{NH}_3)_4\text{I}_2$ ;  $[\text{Zn}(\text{NH}_3)_5]\text{SO}_4$ ;  $\text{Zn}_3\text{AsO}_4 \cdot 2\text{NH}_3 \cdot 3\text{H}_2\text{O}$ ;

$[\text{Zn}(\text{CO} \leftarrow \text{NH}_2)_2]\text{Cl}_2$ ;



$3\text{Hg}(\text{CN})_2, [\text{Fe}(\text{CN})_6]\text{K}_4, \text{H}_2\text{O}$ ;  $\text{Hg}(\text{CN})_2, \text{HgO}$ . The results are given in sixteen curves; the logarithms of the thickness of the layers are plotted against wave-lengths at the limits of absorption. Aqueous solutions of colourless metallic complex salts absorb the light more than those of their simple metallic salts, showing that the formation of the complex ions is responsible for the phenomenon. In general, ammonia complexes are more strongly absorbent than cyanogen complexes. The absorbing power of complex silver salts is no greater than that of simple silver salts, probably due to the fact that  $\text{Ag}^+$  of the simple salts already exists as a complex form of  $\text{Ag}^+$  (compare M. Traube, A., 1886, 661). Cadmium and aluminium complexes are equally as transparent as their corresponding simple salts, as far as the ultra-violet zone is concerned (their plates were sensitive to only  $\lambda = 2000$ ); a hypothesis is given for this peculiarity. All complex salts (except those containing cobalt) give only end absorptions, but not absorption bands; occurrence of the selective absorption depends on the characteristic of metals in the complex. Those complexes containing SCN groups produce selective absorptions, regardless of the kind of metals they contain. In complexes having similar structures, the metals which have greater atomic volumes possess less absorptive power than those having smaller atomic volumes. In complexes containing the same metals, even if their structures may be unknown, it is true that the more components the salt has and the more complex it is, the stronger will be the power of absorption.

## CHEMICAL ABSTRACTS.

**Ultraviolet Absorption of Pyridine,  $\alpha$ -Picoline,  $\beta$ -Picoline, and Piperidine.** ERNST HERRMANN (*Zeitsch. wiss. Photochem.*, 1919, 18, 253—278).—The absorption spectra of pyridine,  $\alpha$ -picoline,  $\beta$ -picoline, and piperidine have been measured in the region  $\lambda\lambda$  2696—3017 for both vapour and alcoholic solutions. For the vapours of pyridine,  $\alpha$ -picoline, and piperidine previous measurements were repeated; in the case of  $\beta$ -picoline the ultra-violet absorption is represented by three broad bands. Series, similar to those observed for benzene derivatives, are evolved. In the  $\alpha$ -picoline spectrum a series of similar structure to one of the pyridine series is observed. In the case of piperidine a structure is observed which is similar to that observed for benzene and is characterised by the appearance of series which may be resolved into typical groups. The spectra obtained from capillary layers of the liquids

and from alcoholic solutions (1 gram-mol. in 20, 100, and 500 c.c. of alcohol) are made up of ill-defined bands. J. F. S.

**Influence of Different Substances on the Absorption of Light by Thin Tungsten Layers.** L. HAMBURGER, G. HOLST, D. LELY, and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1078—1088).—The present paper describes experiments designed to increase the life of tungsten lamps by removal of the tungsten layer produced on the walls of the lamp as it burns. Two classes of substances come under consideration: (i) gases which form less coloured compounds with the tungsten sublimate, and materials which produce these gases; (ii) substances which decolorise the tungsten layer in some way which is probably not chemical. The first group of substances includes chlorine and substances, such as  $K_3TiCl_6$ , which evolve chlorine on heating. This class of substance is reviewed. Experimental work with the second group of substances is described. The light absorption of the tungsten sublimate is decreased when previous to burning the filament is coated with a layer of sodium chloride, sodium phosphate, potassium cyanide, sodium oxide, sodium fluoride, or calcium fluoride. On passing the current through the lamp these substances sublime and are condensed in a non-crystalline condition on the wall of the lamp, and have the effect of increasing the life of the lamp. The action of these substances is not understood, but a discussion is entered into in the paper on the subject. If the deposit is rendered crystalline by the admission of moist air it loses its efficacy. The life of a lamp using sodium chloride is increased 2.6 times, and of one using calcium fluoride 3.3 times. J. F. S.

**A New Photographic Phenomenon.** DONALD NEIL MCARTHUR and ALFRED WALTER STEWART (*T.*, 1919, **115**, 973—974).

**The Secondary Radiation Produced by  $\alpha$ -Rays.** B. BIANC (*Le Radium*, 1919, **11**, 230—234. Compare A., 1913, ii, 371).—By means of an apparatus described, the existence of an ionising radiation ( $\delta$ -rays), produced by impact of  $\alpha$ -rays on glass and metal surfaces, has been clearly put in evidence and the characteristics of the radiation studied.  $\alpha$ -Rays from a polonium surface strike a plate, and the ionisation at various gas pressures produced by secondary radiation from the plate is measured in an ionisation chamber below, the upper surface of which is of wire gauze. The ions produced by the  $\alpha$ -rays are prevented from reaching the ionisation chamber by a suitable electric field. The secondary radiation consists of (1) a small part of the  $\alpha$ -rays reflected, (2) a secondary radiation of the  $\beta$ -type, of velocity  $3 \times 10^9$  cm./sec., which corresponds with a generating potential of 2400 volts; (3) an electronic radiation of feeble velocity ( $\delta$ -rays), completely absorbed by  $0.5 \mu$  of aluminium, and ionising the air over a very limited range, given by  $pa=110$ , where  $p$  is the pressure and  $a$  is the range, both in mm. The number of electrons in (3) is about forty times the number of (2) and about ten times the number of reflected  $\alpha$ -particles. It does not differ greatly with the character of the surface

struck by  $\alpha$ -rays, whether it be of glass or of various metals. Probably these electrons are all emitted with the same velocity, corresponding with about 20 volts, but suffer partial absorption in a very thin film of the generating surface before escaping, so that their actual velocity varies from that corresponding with from 0 to 20 volts.

F. S.

**The Question of the Existence of Isotopes with the same Atomic Weight. The End Products of the Thorium Disintegration Series.** STEFAN MEYER (*Monatsh.*, 1919, 40, 1—14).—The radiation from a specimen of lead, separated by Soddy from Ceylon thorite of atomic weight 207.77, has been examined to test the view whether one of the two isotopes of lead of the same atomic weight, produced as the ultimate products by the branching of the disintegration series, undergoes further change with emission of radiation as yet undetected. The  $\alpha$ -radiation from the lead was found exactly to correspond in intensity with what is to be expected from the polonium regenerated from radium-D, which is necessarily present in this lead, being derived from the small amount of uranium in the original mineral. From a solution of the chloride in water, the polonium was separated by electrolysis on a gold cathode, using a platinum anode, and the range and character of its  $\alpha$ -rays were found to be identical with those of a preparation similarly separated from Joachimsthal pitchblende. The discrepancy between the atomic weight of this lead, 207.77, and what it should be, 208.0, if both end-products are stable, must be explained otherwise than by supposing one of the products to be unstable. There must be 26% of common lead present to account for the difference, or Lawson's hypothesis (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, 126, 723) that there may be a gradual replacement of thorium by uranium in thorium minerals in the earth may be the explanation. There is also no evidence as to what becomes of the product, supposed to be unstable, derived from the composition of thorium minerals. It is known not to change into mercury or bismuth, and the existence of any large quantity of an isotope of polonium in thorium minerals is also excluded by the evidence. As regards thallium, Exner and Haschek have found considerable quantities by the spectroscope in Cornish pitchblende, but Hoernes, in a careful analysis of 1 kilogram of thorium-rich, but uranium-poor, monazite could not detect thallium, so that it is probable that its presence in uranium and thorium minerals is accidental, not genetic. A review of the whole of the cases where two isotopes of the same atomic weight are supposed to occur by branching of the series leads to the conclusion that there is no certain instance of this known, and that both the end-products of thorium are stable forms of lead of the same atomic weight, and therefore indistinguishable from one another.

F. S.

**Is the Electrical Conductivity of the Elements Conditioned by the Presence of Isotopes?** F. H. LORING (*Chem. News*, 1919, 119, 62—64. Compare this vol., ii, 313).—When the

isotopic percentages previously given (*loc. cit.*) are plotted against the resistivities of a number of metals, a straight line curve is obtained, which implies that there is a foundation for the theory of whole-number isotopes as applied to ordinary elements. Cadmium constitutes the only exception to this rule, but this may be attributed to the unconfirmed peculiarity in the temperature-resistance curve of this element. The theory of conduction is of interest in connexion with the above-mentioned relationship. Thus, if a small-mass nucleus is so close to a large-mass nucleus that the electronic orbits combine to form a figure of eight, the electrons tending to leave the former to pass round the latter, owing to the greater attraction of the larger mass, then overloading the circuit electrically at any point might give rise to a progressive flow of electrons from atom to atom. On cooling the metal, a point might be reached when further cooling would not improve the contiguity of the orbits, so that perfect conductivity of electricity without any oscillation or vibration of the atoms might take place at a temperature just above absolute zero.

J. F. S.

**Behaviour of Non-aqueous Solutions of Salts.** A. THIEL (*Zeitsch. Elektrochem.*, 1919, 25, 214).—Polemical against Beutner (this vol., ii, 263), in which the author maintains that the reasons advanced to explain the electrical conductivity of salts in non-aqueous solvents do not clear up the difficulty, and are not justified on the data put forward.

J. F. S.

**Activities of the Ions of Strong Electrolytes.** DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1919, 41, 1086—1092).—A theoretical paper in which it is shown that, since the product of the transport number of the chloride ion and the equivalent conductivity is a constant at a given concentration and temperature for the chlorides of the alkali metals and hydrogen, it may be assumed that the activity of the chloride ion in these solutions is also independent of the nature of the positive univalent ion. On this basis, the activity coefficients of both ions of hydrochloric acid have been calculated for concentrations between 0.001665*N* and 0.100*N*. The potential of the normal hydrogen electrode against the normal calomel electrode has also been calculated, and the value  $E = 0.2828$  volt obtained.

J. F. S.

**Generation of Electricity by Atomising Liquids.** (Ballot-electricity). IV. C. CHRISTIANSEN (*Ann. Physik*, 1919, [iv], 59, 95—100. Compare A., 1916, ii, 75).—A continuation of previously published work undertaken with the object of ascertaining whether isomerides produce the same electric effect when projected against an electrode in a finely atomised stream. The experiments show that *d*-tartaric acid, *l*-tartaric acid, *i*-tartaric acid, and racemic acid in *N*/10-solution produce exactly the same effect, which is very small and approximates in value to that of the inorganic acids. When the above-mentioned acids are mixed with

alcohol or 2*N*-sodium chloride, the effect is much greater in each case; in the case of the alcohol mixtures, the value is the same for each acid, but with the sodium chloride mixtures the values vary slightly. Propionic acid produces a much greater effect than either of the monochloro-substitution products. Propionic acid and  $\alpha$ -chloropropionic acid produce a positive effect, whilst  $\beta$ -chloropropionic acid produces a negative effect. The  $\beta$ -compound does not change its effect on keeping, but the  $\alpha$ -compound has a decreased effect on keeping.  $\beta$ -Hydroxybutyric acid in *N*/2-solution has a much larger effect than  $\alpha$ -hydroxybutyric acid. Substitution of bromine has a different effect than substitution of chlorine on the ballo-electric effect of organic substances. This fact is shown by experiments with bromal hydrate, chloral hydrate, monochloroacetic acid, and monobromoacetic acid. J. F. S.

**Generation of Electricity by Atomising Liquids (Ballo-electricity).** V. C. CHRISTIANSEN (*Ann. Physik*, 1919, [iv], 59, 280—292. Compare preceding abstract).—An instrument (ballo-meter) is described whereby the charge on particles of a liquid atomised in air, the charge on the air, and the amount of electricity which has escaped from the particles which have been in contact may be measured. J. F. S.

**The Electrolytic Potential of Copper in the Presence of Various Electrolytes.** P. BENVENUTI (*Atti R. Ist. Veneto Sci.*, 1916, 75, 1317—1329).—This work was started with the idea of producing an electrolytic deposit of an alloy of copper and manganese, but this was afterwards given up as impossible, and the measurements of the potential of copper in the presence of various electrolytes were systematically continued on account of the information thus obtained in regard to the greater or less stability of the complexes produced in this way, and because the data obtained could be utilised in further investigations. The method consisted in connecting the copper electrode, and the electrolyte in which it was immersed, with a normal calomel electrode, and in measuring the *E.M.F.* of the resulting cell by Poggendorff's compensation method. Measurements were made at 15°. The salt of copper was the sulphate. The copper electrode was immersed in this solution with varying quantities of other electrolytes. The results show that, by the addition of these other substances, the potential of the copper increases in the electropositive direction in proportion to the formation of complex ions. In proportion to the increased stability of the complex ions formed, the electrolytes studied arranged themselves in the following order: sodium formate, sodium acetate, ammonium tartrate, hydrochloric acid, potassium bromide, sodium thiosulphate, and potassium cyanide. The author believes that a more extensive study of these phenomena will reveal interesting relations between the nature of electrolytes co-existing in one solution and the stability of the complexes which are formed.

CHEMICAL ABSTRACTS

**Phenomenon of Electrical Supertension. II.** A. SMITS  
(*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 1106—1111.  
Compare this vol., ii, 8, 91).—A theoretical paper in which the  
conditions of the supertension of hydrogen generated when metals  
act on water are considered on the basis of the phase rule.

J. F. S.

**Electrolytic Reduction of Arsenic and Arsenious Acids to  
Arsenic Trihydride at Cathodes of Different Metals.**

LEWIG RAMBERG (*Lunds. Univ. Arsskr.*, N.F., Abt. 2, 1918,  
14, No. 21, 1—47; from *Chem. Zentr.*, 1919, i, 905—906).  
—A historical résumé of the literature is given, and the newer,  
quantitative methods are critically discussed. The latter are all  
unsatisfactory. The discrepancies between the data of various  
authors are due partly to deficient technique and partly to the  
unexpectedly great influence of the nature of the surface of the  
cathode. Certain new types of electrolytic apparatus are  
described which are chiefly notable for the type and location of  
the diaphragm. The errors due to the diffusion of com-  
pounds of arsenic and to the wandering of the arsenate ion to  
the anode, together with their dependence on the nature of the  
material of the diaphragm, have been investigated. It is found  
that the wandering of the ions is a considerably more important  
factor than is diffusion, and is so important that the quantitative  
reduction of arsenic acid to arsenic trihydride can only be effected  
at cathodes at which the process occurs very rapidly. Arsenic  
trihydride is estimated by absorption in standard iodine solution  
and estimation of excess of the latter with standard arsenious  
acid.

Cathodes of the following metals have been used: mercury,  
zinc, copper, silver, lead, iron, tin, cadmium, nickel, and platinum.  
The results are given in a series of tables, from which it appears  
that the nature of the cathodic surface has a great influence on  
the reduction of arsenic acid to arsenic trihydride. The process  
generally takes place far more rapidly at spongy than at polished  
surfaces. The nature of the surface appears to be less important  
in the case of arsenious acid, and in any case the polished surfaces  
are not less effective than the spongy ones.

Different series are obtained for arsenic and arsenious acids  
when the metals are arranged in order of reducing power, but  
without regard to their superficial condition. In no case does the  
order exactly coincide with that derived from consideration of  
the voltage, although a certain parallelism exists between the latter  
and the power of reducing arsenious acid.

Rapid and complete reduction of arsenic acid to arsenic tri-  
hydride only occurs at mercury cathodes, although certain  
amalgamated metals give moderately useful results. On the other  
hand, a mercury cathode is unsuitable for the reduction of con-  
siderable amounts of arsenious acid, since the arsenic is not hydro-  
lysed as rapidly as it is formed: a solid phase of arsenic or



arsenic amalgam is thus formed which is only very slowly transformed into arsenic trihydride.

The practical value of the methods is demonstrated by a series of analyses. Estimation of arsenic acid, in amounts containing as much as 50 mg. of arsenic, can be readily effected at mercury cathodes with an error of  $\pm 0.1\%$ . Cathodes of lead, silver, or tin are most useful in the estimation of arsenious acid. The supposed superiority of lead for this purpose is not confirmed, and polished tin appears to be the best material. The same accuracy as in the estimation of arsenic acid at mercury cathodes cannot, however, be attained; with increasing quantities of arsenic, the losses become greater, and reach as much as  $0.25\%$  with 20 mg. of arsenic.

H. W.

**Removal of Residual Gases, especially from the Electric Glow Lamp.** L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 1062—1077).—By determination of the changes in gas pressure and by spectroscopic observations, it is shown that with the aid of electric discharges phosphorus vapour can be made to react rapidly with all gases except the inert gases. The action observed in the glow-lamp with phosphorus can also be observed with silicates. At high temperatures, silicates undergo fractional distillation. When tungsten and silicates are in contact at a high temperature, a reaction takes place between them by which an alkali metal is liberated. By means of this, as in the case of phosphorus, the residual gases can be removed from glow-lamps with the aid of electric discharges. The reaction between tungsten and glass makes possible the use of this metal for "leading-in" wires. When rapidly cooled, the vaporised silicate has properties different from those of the normal glass, since it is in a supercooled condition, and this condensate can decrease the blackening of the wall of the lamp produced by the vaporised tungsten. If, instead of coating the filament with a silicate, an aluminate, calcium phosphate, magnesium oxide, or silica is substituted, a similar reaction occurs. In the case of silica, it is to be assumed that a trace of free silicon is formed; only quantities of the order  $0.001$  mg. of silicon show a detectable activity.

J. F. S.

**Specific Heat of Argon and Several Polyatomic Gases.** WILHELM HEUSE (*Ann. Physik*, 1919, [iv], 59, 86—94).—Making use of the method previously employed (A., 1912, ii, 19; 1913, ii, 183), the author has determined the specific heat of argon, carbon dioxide, nitrous oxide, nitric oxide, methane, acetylene, ethylene, and ethane at temperatures varying from the ordinary temperature to within a few degrees of the condensation point. The following values, among others, have been obtained: argon,  $c_p$   $15^\circ$ ,  $0.531$ ;  $-182^\circ$ ,  $0.556$ ; carbon dioxide,  $c_p$   $20^\circ$ ,  $0.846$ ;  $-75^\circ$ ,  $0.768$ ; nitrous oxide,  $c_p$   $20^\circ$ ,  $0.879$ ;  $-30^\circ$ ,  $0.835$ ;  $-70^\circ$ ,  $0.797$ ; nitric oxide,  $c_p$   $15^\circ$ ,  $1.012$ ;  $-45^\circ$ ,  $1.001$ ;  $-55^\circ$ ,  $1.014$ ;  $-80^\circ$ ,  $1.024$ ; methane,  $c_p$   $15^\circ$ ,  $2.22$ ;  $5^\circ$ ,  $2.20$ ;  $-30^\circ$ ,  $2.13$ ;  $-55^\circ$ .

11;  $-80^{\circ}$ , 2.11; acetylene,  $c_p$   $18^{\circ}$ , 1.680;  $-71^{\circ}$ , 1.470; ethylene,  $c_p$   $18^{\circ}$ , 1.527;  $-36^{\circ}$ , 1.371;  $-68^{\circ}$ , 1.314;  $-91^{\circ}$ , 1.291; ethane,  $c_p$   $15^{\circ}$ , 1.728;  $-35^{\circ}$ , 1.539;  $-82^{\circ}$ , 1.455. In a large table, the values of the density, specific and molecular heats at constant pressure and constant volume, and the ratio of the specific heats at various temperatures and at zero, are tabulated. J. F. S.

### Some Molecular Heats at Very High Temperatures.

H. von WARTENBERG and G. WITZEL (*Zeitsch. Elektrochem.*, 1919, 25, 209—212).—The molecular heats of the oxides of magnesium, calcium, and aluminium have been determined by burning a mixture of the metal and its oxide in oxygen in a calorimetric bomb. The temperature at which the measurements are made is that of the melting point of the oxide, and this is obtained by using such a mixture of oxide and metal that the oxide is just not melted. Instead of using the oxide as indicator, a mixture of the metal under investigation and finely divided platinum or iridium may be used in such quantities that the metal is just melted. The results obtained represent the upper limit, and are probably accurate to 10—20%; regarded in this way, they are in agreement with the value extrapolated from the curve of values up to  $1600^{\circ}$ . The following values have been obtained: magnesium oxide, 11.6 cal. at  $2780^{\circ}$ ; calcium oxide, 14.8 cal. at  $2552^{\circ}$ ; and aluminium oxide, 29.1 cal. at  $2030^{\circ}$ . J. F. S.

### The Molecular Heat of Binary Metallic Alloys.

Augusto LEVI (*Atti R. Ist. Veneto Sci.*, 1916, 75, 627—632).—The principle of Dolezalek-Schulze for calculating the molecular refraction of binary liquid mixtures is applied to the calculation of the molecular heat of bismuth-tin alloys.  $p_a$  and  $p_b$  are the masses of the constituents in a gram of the mixture,  $m_a$  and  $m_b$  the molecular weights, and  $q_a$  and  $q_b$  the molecular fractions of the constituents.

$$q_a = (p_a/m_a) / [(p_a/m_a) + (1 - p_a)/m_b],$$

$$q_b = [(1 - p_a)/m_b] / [(p_a/m_a) + (1 - p_a)/m_b].$$

If  $C_{ab}$  is the specific heat of the mixture, (1)  $C_{ab} = C_a p_a + C_b p_b$ , and for the molecular heat of the mixture, (2)  $C_{ab} (m_a p_a + m_b p_b) = C_a m_a q_a + C_b m_b q_b$ , in which the first member expresses the molecular heat of the mixture as found by experiment, and the second member the value as calculated by the rule of mixtures. Experiments were carried out by the method of mixtures with alloys of lead and of tin with bismuth. Data indicate clearly the formation of a compound of lead and bismuth when the molecular fraction of lead is 0.44. The eutectic is identical with or close to that mixture which gives maximal molecular heat and produces a compound in the alloy. The curve for mixtures of tin and bismuth is more difficult to interpret and suggests further investigation.

CHEMICAL ABSTRACTS.

**Latent Heat and Surface Energy. I.** D. L. HAMMICK (*Phil. Mag.*, 1919, [vi], 38, 240—245).—The author has deduced an

expression connecting the molecular surface energy with the latent heat. This has the form  $\rho V/d = L_1 J/6$ , in which  $\rho$  is the surface energy in ergs per sq. cm.,  $V$  is the molecular volume,  $d$  the molecular diameter,  $L_1$  the internal latent heat per gram-mol. in cal., and  $J$  the mechanical equivalent of heat. This equation has been evaluated for a number of gases (6) and organic liquids (23), and is shown to fit the facts remarkably well. A table of the mean diameter of the molecules of the substances concerned is given containing the value deduced from the diffusion, thermal conductivity, refractive index, and the Avogadro constant  $b$ .

J. F. S.

### Temperature of Explosion for Endothermic Substances.

RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (T., 1919, 115, 1006—1010).

**Calculation of the Relation between the Vapour Pressure of a Solid and that of a Supercooled Liquid at Various Temperatures.** A. BOUTARIC (*Compt. rend.*, 1919, 169, 432—435).

The formula given is  $\log_e p_1/p_2 = U_s/2RT \times 1 - T^2/\theta^2$ , where  $p_1$  and  $p_2$  are the vapour pressures of the supercooled liquid and solid respectively at  $T^\circ$  (absolute),  $\theta$  the temperature of transformation, and  $U_s$  the diminution of total energy at this temperature. In the case of water and benzene, the observed and calculated values agree with one another, but there is a considerable difference between the values for formic acid.

W. P. S.

### Dependence of the Vapour Tension of Benzene-Toluene Mixtures on the Temperature.

ALFRED SCHULZE (*Ann. Physik*, 1919, [iv], 59, 73—85).—Making use of the vapour pressure measurements of Mangolt (*Sitzungsber. K. Akad. Wiss. Wien*, 1893, 102, 1071) for mixtures of benzene and toluene, the author has plotted the vapour pressure as a function of the molecular concentration for the temperatures 20°, 30°, 40°, 50°, and 60°. The partial pressures of both constituents are also calculated and plotted. A consideration of the curves, based on the law of mass action, allows conclusions on the molecular complexity of toluene to be drawn. It is shown that at 20° liquid toluene consists of double molecules to the extent of 50%, at 50° to the extent of 8%, and at 60° it is unimolecular.

J. F. S.

### Vapour Pressure and Affinity of Isotopes.

F. A. LINDEMANN (*Phil. Mag.*, 1919, [vi], 38, 173—181. Compare this vol., ii, 209).—Though isotopes in principle must be separable both by fractionation and by chemical means, the amount of separation to be expected depends on the way the chemical constant is calculated, and experiments on the vapour pressure and affinity of isotopes would give valuable information on this point. F. S.

### The Possibility of Separating Isotopes.

S. CHAPMAN (*Phil. Mag.*, 1919, [vi], 38, 182—186).—A method of separating a mixture of gaseous isotopes, depending on thermal diffusion, is sug-

rested, and from the mathematical examination of the problem it is concluded that it should prove practicable. If the mixture is kept in two communicating vessels maintained at different temperatures, in the equilibrium condition there is a slight excess of the heavier gas in the colder vessel. For the case of a mixture of equal volumes of neon of molecular weight 20 and of the hypothetical meta-neon of molecular weight 22, supposing the mixture to be contained in two bulbs at absolute temperatures  $80^\circ$  and  $300^\circ$ , the cold bulb would contain in equilibrium 48.9% of the meta-neon and 51.1% of neon. This difference of 2.2% is reduced to 1.2% when the proportions of the mixture are as 10:1, and assumes the molecules to behave as elastic spheres. The time taken for the equilibrium to be reached ought not to be unduly protracted, and the operation can be repeated as often as desired on the fractions obtained.

F. S.

**Free Energy of Dilution of Aqueous Sodium Chloride Solutions.** ARTHUR JOHN ALLMAND and WILFRID GUSTAV POLACK (T., 1919, 115, 1020—1039).

**Connexion between the Atomic Weights, Densities, and Heats of Reaction of the Elements. II.** KARL FEHRLE (*Physikal. Zeitsch.*, 1919, 20, 330—342. Compare A., 1918, ii, 296).—The formula put forward previously (*loc. cit.*) for calculating the heat of formation of compounds from the molecular weight and the density has been used to calculate the heat of formation of the chlorides, bromides, iodides, oxides, and carbonates of a number of elements of groups I—V. The results indicate that the formula gives values which are in moderate agreement with the experimental values.

J. F. S.

**Vapour Pressures and Densities of Mixtures of Acetone and Methyl Ethyl Ketone.** TUDOR WILLIAMS PRICE (T., 1919, 115, 1116—1126).

**Density and Temperature. II.** W. HERZ (*Zeitsch. Elektrochem.*, 1919, 25, 215—216. Compare this vol., ii, 268).—The author has calculated the density at the absolute zero ( $d_0$ ) from the values at the critical temperature ( $d_{crit}$ ), boiling point ( $d_b$ ), freezing point ( $d_m$ ), and at  $20^\circ$  respectively for a number of alcohols (8), esters (13), acids (9), hydrocarbons (13), and halogen-substituted hydrocarbons (4) by means of the formulae  $d_0 = 3.75d_{crit}$ ,  $d_0 = 1.41d_b$ ,  $d_0 = 1.21d_m$ , and  $d_0 = d_t(0.77 + 0.64T/T_{crit})$ .

The values obtained by the various methods are in fair agreement with one another. The density at absolute zero decreases with increasing molecular weight in the series of alcohols, acids, esters, and aromatic hydrocarbons, but rises with increase of molecular weight in the series of paraffins and halogenated benzenes.

J. F. S.

**Are the Divergencies of the Atomic Weights from Whole Numbers to be Explained by Isotopy?** O. STERN and M. VOLMER (*Ann. Physik*, 1919, [iv], 59, 225—238).—Experiments are described in which hydrogen and oxygen respectively are generated and the gas allowed to diffuse under atmospheric pressure. The density of the gas is determined before and after a portion has diffused. In this way, it is shown that the whole of the gas has the same density, that is, hydrogen and oxygen are not mixtures of isotopes. It is also shown that every theory of the structure of atoms, based on the Prout hypothesis, must be capable of explaining the divergence of the atomic weights from whole numbers by means of energy differences. J. F. S.

**Solubility. III. Relative Values of Internal Pressures and their Practical Application.** JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1919, 21, 1067—1080. Compare A., 1916, ii, 518; 1918, ii, 36).—Various independent methods are discussed for calculating the internal pressures of liquids, and although the values obtained differ considerably, yet they are found to be closely parallel. Tables of the relative values are given in the paper for non-polar substances. Other substances may be tabulated with reference to these substances by knowing their densities, together with either surface tension, boiling point, the constant  $a$  of the van der Waals' equation, the coefficient of expansion, or the last together with the compressibility. The use of these values is discussed in connexion with predictions concerning the solubilities of solids, liquids, and gases, the distillation of liquid mixtures, molecular weights and association, deviations from the law of mass action, partition coefficients, and the choice of solvent in recrystallisation. J. F. S.

**Adsorption Isotherm at Low Concentrations.** A. M. WILLIAMS (*Proc. Roy. Soc. Edin.*, 1919, 39, 48—55).—A theoretical paper in which it is shown that for very small adsorptions the adsorption law has the form  $a = a_0 c$  for both gases and solutions. From this expression, adsorption curves have been produced for solutions and found to agree with the curves obtained by Trouton for acetic acid and charcoal (*Rep. Brit. Assoc.*, 1911, 328) and Schmidt-Walter for water, benzene, and toluene (*A.*, 1914, ii, 542). J. F. S.

**Surface Tension and Chemical Interaction.** G. N. ANTONOFF (*Phil. Mag.*, 1919, [vi], 38, 417—419. Compare A., 1918, ii, 437).—A theoretical paper in which it is shown that the results obtained in the previous paper (*loc. cit.*) can be obtained whatever law of molecular action is used as the basis of calculation. The results previously obtained depend on the assumption that molecular action takes place according to an inverse fourth-power law. It is now shown that if an inverse  $n$ th power law be assumed, the expressions for surface tension ( $\alpha$ ) and internal

pressure ( $P$ ), respectively, would be  $\alpha = kp^{(n+1)/3}$  and  $P = 2kp^{(n+2)/3}$ . Thus the formula connecting both quantities is  $P = k\alpha p^{1/3}$ , where  $k=2$ , as in the previous paper. The relationship  $\alpha_2 = \alpha_1 - \alpha_2$  does not depend on the law of molecular attraction, but is a result of a certain chemical interaction between the liquids forming the solutions which enables the heterogeneous system to become stable and prevents both layers from mixing.

J. F. S.

**Diffusion of Double Salts.** D. MERRILL TORRANCE (*Chem. News*, 1919, 119, 66—67).—From experiments on the rate of diffusion of potassium antimonyl tartrate and potassium sodium tartrate, it is shown that the antimony does not diffuse through with three times the velocity of the potassium, as was expected. The experiments also show that the rate of diffusion through dead or artificial tissue is very different from that through living tissue.

J. F. S.

**Velocity of Diffusion.** HANS BAUER (*Physikal. Zeitsch.*, 1919, 20, 339—340).—Polemical. A number of remarks to the work of Franks (this vol., ii, 100) on the same subject.

J. F. S.

**Reactivity of Powdered Glasses.** PAUL NICOLARDOT (*Compt. rend.*, 1919, 169, 335—337).—Account must be taken of the degree of fineness of the powder in testing the resistance of glass to solvent action by boiling the powdered material with water and with dilute hydrochloric acid, otherwise concordant results will not be obtained. Powders of various sorts of glass were prepared in three degrees of fineness by sifting, the ratios of the surfaces being substantially 1:2.84:12.8, and the loss in weight of each after boiling in a platinum vessel for three hours with pure water and with  $N/10$ -hydrochloric acid was determined. From the tables given, the following examples may be quoted, the figures being the loss per 1000 of the whole glass and the three powders mentioned above:

|                                |                          |
|--------------------------------|--------------------------|
| Jena glass to water.           | 0.09, 0.25, 0.75, 2.75.  |
| " " $N/10$ -HCl.               | 0.03, 2.00, 5.25, 40.25. |
| Thuringian (R) glass to water. | 0.03, 0.25, 0.75, 5.25.  |
| " " $N/10$ -HCl.               | 0.01, 0.75, 3.75, 12.50. |
| A French glass to water.       | 0.11, 1.00, 2.00, 10.00. |
| " " $N/10$ -HCl.               | 0.02, 0.25, 1.75, 17.00. |

It will be seen that, contrary to observations on the whole glass, the powder in nearly all cases is attacked more by hydrochloric acid than by water. Further, whilst water attacks powders of different fineness to practically the same extent per unit of exposed surface, the diluted hydrochloric acid in general attacks the finest powder more vigorously than the others in proportion to its surface area.

G. F. M.

**Influence of Neutral Chlorides on Chromium Chloride Solutions.** M. E. BALDWIN (*J. Amer. Leather Chem. Assoc.*, 1919, 14, 10—19; from *Chem. Zentr.*, 1919, i, 805—806).—It has

been previously shown (Thomas and Baldwin, *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 192, 248) that the acidity of solutions of chromium sulphate, determined by the electrometric process, is increased by addition of chlorides and is primarily diminished, but subsequently raised by addition of sulphates. The influence of the chlorides of sodium, potassium, ammonium, lithium, and barium on the acidity of solutions of chromium chloride has now been investigated, the experiments being conducted immediately after preparation of the solutions and also after preservation during fifty days. The results show that the hydrogen-ion concentration of chromium chloride solutions is increased by the presence of neutral chlorides, although the total amount of acid hydrogen remains constant. When the salts are arranged in order of increasing effect, the following series is obtained:  $(\text{KCl}, \text{NH}_4\text{Cl})$ ,  $\text{NaCl}$ ,  $\text{LiCl}$ ,  $\text{BaCl}_2$ . To determine whether the hydrolysis of chromium chloride plays a part in these results, a similar series of experiments has been conducted with hydrochloric acid solutions of approximately the same hydrogen-ion concentration, when similar effects are observed. It is noticeable that the different salts increase the hydrogen-ion concentration in proportion to their capacity of uniting with a larger number of molecules of water in accordance with the theory of hydrates. Comparison of the results obtained with solutions of chromium chloride and hydrochloric acid show that the phenomenon does not depend on the hydrolysis of the former, since the changes in either case are of the same order and approximately of the same magnitude. On the other hand, the changes which occur after some time in the "actual acidity" of chromium chloride solutions appear to depend on the nature and amount of chromium chloride present. An explanation of the increase in the hydrogen-ion concentration of chromium chloride solutions caused by the addition of neutral chlorides has been advanced by Wilson and Kern (*J. Amer. Leather Chem. Assoc.*, 1917, **12**, 455), who suppose that the amount of water available as solvent is diminished by the combination of the salts and their ions with a portion of the water. H. W.

**Isomeric Alloys.** G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 332—350; from *Chem. Zentr.*, 1919, iii, 89—90). —Normal distribution of atoms cannot occur when two metals separate simultaneously at a temperature at which diffusion is impossible in the mixed crystal; in these circumstances, the arrangement is probably irregular. The crystalline or crypto-crystalline products obtained when two metals separate from a solution have been investigated to some extent, but exact comparison with the series of alloys obtained from the molten metals has not previously been possible, since the properties of the latter were only incompletely known. Binary, crystalline, metallic mixtures can be obtained from galvanic cells formed by placing the two metals in a solution of the less noble, by the electrolysis of a solution of the two metals, by precipitation of the one metal on the

other, and by reduction of the solution of the two metals. Before comparing the properties of these mixtures with those obtained from molten masses, it is desirable to obtain an idea of the capacity for diffusion of a metal deposited on a cathode of a second metal; this power is a characteristic of the nascent atom, and is to be distinguished from the mobility of two kinds of atom in a mixed crystal. If a cell consisting of the two metals immersed in a solution of the less noble metal is short-circuited, cations of the latter are deposited on the more noble metal. If, now, diffusion proceeds at a negligible rate, the original potential of the cell is rapidly regained when the circuit is opened; when diffusion is more rapid, the recovery is gradual. If the potentials are measured by the electrometer, the method gives a very sensitive means of detecting diffusion of the less noble into the nobler metal. Solutions of cadmium and copper sulphates have been electrolysed with the object of obtaining information of the effect of the composition of a mixed electrolyte and of the current density on the composition of the cathodic deposit. By suitable variation of these factors, deposits can be obtained the tensions of which vary between zero and the tension of copper towards cadmium. The Cu-Cd alloys obtained from the molten metals behave quite differently, and therefore cannot be identical with the mixtures prepared electrolytically. The relative affinity of the two metals governs the content of precipitating metal in the precipitated metal. When the two metals can unite with one another, the deposit of the nobler metal from the solution is rich in less noble metal; when, however, a compound is not formed, the noble metal is deposited either free from or admixed with but small amounts of the less noble metal. In certain cases, the composition of the precipitate corresponds with that of one of the compounds obtained from the molten mixtures (for example,  $\text{Cu}_3\text{Cd}_3$ ,  $\text{CuCd}_3$ ,  $\text{Cu}_3\text{Sn}$ ); with other pairs of metals, the composition of the precipitates varies greatly in different preparations (with Cu-Zn, Ag-Zn, Ag-Cd). Even in those cases (Cu-Au, Fe-Pt) in which the two metals form a continuous series of mixed crystals from their molten mixtures, the precipitate is rich in the less noble metal. The precipitates from less noble metals appear to be identical with those obtained by the electrolysis of mixed electrolytes; in each case, the composition depends on that of the electrolytes and on the current density at the place of precipitation. The alloys obtained from molten metals are not identical with those prepared by precipitation from mixed electrolytes; this is shown in detail in the cases of  $\text{Cu}_3\text{-Sn}$ ,  $\text{Au-Ag}$ ,  $\text{Zn-Cu}$ .  
H. W.

**Alteration in the Chemical Behaviour of Metals and their Mixed Crystals by Mechanical Working.** G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 351--361; from *Chem. Zentr.*, 1919, iii, 90--91).--The energy content of a piece of metal is increased by cold working; the methods of estimating this increase are described. Permanent deformation of a piece of metal



causes an increase in its energy which depends on the extent of deformation, the degree of working, and also on the nature and temperature of the metal. The mechanical process leads to a disintegration of the metal which corresponds with an increase in potential energy, whilst the latter is also augmented by processes which can occur within the atom itself. A cold-worked metal is less noble in the hard than in the soft condition. Since those layers which lie on the surface are alone affected, a piece of metal which is superficially hardened, but internally still soft, can behave as less noble than a thoroughly hardened piece. These conclusions have been verified by observations on silver wires which had been worked in different manners. The supposedly exceptional position of bismuth could not be confirmed. The increase in the rate of solution of iron caused by cold-working is probably due to the formation of twin lamellæ in the iron crystals. The action limits of chemical reagents on alloys of gold with copper and silver are altered by mechanical working of the alloys. Rolling and hammering imparts increased chemical activity to Ag-Au alloys, which is noticeable when the gold content is far greater than that which corresponds with the reaction limit in soft alloys. Polishing of the alloys has an effect similar to that of converting them into thin foil. The unexpectedly great displacement of the action limits by mechanical working can only be explained by the assumption of an alteration in the properties of the gold atoms; the latter, in consequence of displacement, are much less firmly retained than formerly, and consequently separate more readily from the lattice after removal of the active atoms. An agent, the action of which surpasses the natural limit, is able to remove the protecting gold atoms from the lattice when their number corresponds with that of the normal reaction limit.

H. W.

#### Atomic Structures of Non-metallic Mixed Crystals.

G. TAMMANN [with K. W. SCHMIDT] (*Nachr. Ges. Wiss. Göttingen*, 1918, 296—318; from *Chem. Zentr.*, 1919, i, 782—784).

—In the absence of abnormal double refraction, the occurrence of definite reaction limits enables the distinction to be made between normal and irregular distribution. The phenomenon has been utilised for the purpose of gaining insight into the arrangement of the molecules in non-metallic mixed crystals. The capacity for diffusion of the two components must also be taken into account, since conclusions, based on the absence of reaction limits, are only valid when the diffusion is negligibly small. Reaction limits similar to those observed with metals occur in mixed crystals of salts when they are prepared from the molten materials and tempered for a sufficient period. The action of water on mixed crystals of sodium and silver chlorides has been investigated, both salts being completely miscible in all proportions in the liquid and crystalline conditions. Crystals with 1—0.75 mol. AgCl scarcely yield any sodium chloride to water; those with 0.75—0.625 mol. AgCl give part of the salt, whilst water removes the sodium

chloride completely from those containing 0.625 mol. AgCl and less. The observations thus closely resemble those made on the extraction of Au-Cu and Au-Ag alloys with boiling nitric acid. An explanation of the behaviour of the salts is based on a conception of the distribution of the silver, sodium, and chlorine atoms in the space lattice. This is determined for sodium chloride by means of the Röntgen spectrum, and since sodium chloride and silver chloride form an unbroken series of mixed crystals, a similar lattice may be assigned to the latter. The normal distribution of the different atoms in the assumed structure is indicated for the molar fractions  $5/8$  and  $6/8$ . Diffusion in mixed crystals shows important quantitative differences from that observed with metals. In the neighbourhood of the melting point, the process occurs much more rapidly in metallic than in non-metallic mixed crystals, and is also more noticeable at temperatures considerably below the melting point. This dictum is not based on quantitative determination of the rate of diffusion, but depends on phenomena (such as the rapidity with which layers of mixed crystals become homogeneous), from which an idea of the rate of diffusion can be obtained. Mixed crystals, the content of which in inactive material is greater than that of the reaction limit at high temperature, deposit a portion of the active material as a result of diffusion, the process occurring more rapidly with increasing temperature. If crystalline powders of two substances, one of which is colourless and the other coloured, are pressed together, an idea of the relative rates of diffusion can be obtained by observation of the change in colour at the originally sharp line of contact. With electrolytes, the conductivity, with similar drop in voltage, is a measure of the mobility of the ions involved in the process. Noticeable electrolytic conductivity is an indication of incipient diffusion. With increasing temperature, the conductivity increases from negligible to very considerable values near the melting point. The great differences in the relative rates of diffusion in metallic and non-metallic mixed crystals are shown by the fact that definite reaction limits are much more rapidly developed by tempering with the former than with the latter. The diffusion of compressed substances has been investigated with the following pairs of compounds: dibenzyl and azobenzene, stilbene and azobenzene, sodium sulphate decahydrate and sodium chromate, potassium perchlorate and potassium permanganate, magnesium sulphate heptahydrate and nickel sulphate heptahydrate, mercuric bromide and mercuric iodide decahydrate. Diffusion of the coloured into the colourless substance is only noticeable with isomorphous crystals, the melting points of which are only slightly higher than the temperature of the experiment; even when this is the case, the process only occurs very slowly. The application of the laws of dilute solution to the solubility and vapour tension isotherms of series of mixed crystals is discussed, but the application of the theory is rendered impossible, since equilibrium between solution and mixed crystal is not attained in any reasonable time when equilibrium is deduced

from the normal arrangement of the crystal lattice. Differences in distribution in the lattice cause mixed crystals of similar composition to form normal and abnormal isomerides, which are differently attacked by solutions. Thus mixed crystals of silver and sodium nitrates were prepared (1) by very slowly cooling a mixture of the molten salts, and (2) by cooling a solution of the two salts in aqueous alcohol. When the two products were treated with a saturated solution of sodium nitrate, considerably greater amounts of silver nitrate were dissolved from the latter than from the former. A second example of isomeric mixed crystals occurs with the chlorides of silver and sodium; they are distinguished by the difference in the rates at which sulphide is formed on them by the action of a solution of sodium chloride containing ammonium sulphide.

H. W.

**Chemical and Galvanic Properties of Mixed Crystals and their Atomic Structure.** G. TAMMANN (*Zeitsch. anorg. Chem.*, 1919, 107, 1-239).—A detailed account is given of the author's previously published researches on the discontinuous properties of mixed crystals, and particularly of simple binary alloys, an explanation of these properties in terms of the space-lattice theory being fully discussed. (Compare A., 1917, ii, 448; 1918, ii, 209, 225, 235, 443, 445, 447.)

E. H. R.

**Method of Growing Large Crystals from Solution.** R. W. MOORE (*J. Amer. Chem. Soc.*, 1919, 41, 1060-1066).—The author has produced perfect crystals of potassium sodium tartrate nearly 10 cm. long by the following method. A saturated solution at 35-40° was made up, removed from the excess of solid, heated to 7-8° above the saturation temperature, and rapidly filtered through paper, care being taken that the temperature did not fall to less than 4-5° above the saturation temperature. Small seed crystals are suspended on threads in a jar and the salt solution poured in. The jar is covered with a glass plate and placed in a water-bath 0.5° above the saturation temperature of the solution. The temperature is allowed to fall to the saturation temperature, and then by means of a sensitive thermo-regulator the rate of cooling is regulated to 0.1° per day until the crystals have become perfect. This usually requires one day. Then the temperature is allowed to fall 0.2° per day until the crystals are 1.8-2.5 cm. long, after which the rate of cooling is increased to 0.5-0.6° per day. When the bath has reached the ordinary temperature the crystals are removed and dried by wiping with a soft cloth.

J. F. S.

**The Effect of Ions of Sodium Chloride and Calcium Chloride on the Electrical Conductivity of Certain Colloidal Mixtures.** NEWTON BALDWIN GREEN (*Plant World*, 1918, 21, 303-317).—Cylinders of colloidal gel, such as gelatin, or mixtures of gelatin, agar, and whole wheat flour, are readily penetrated by the ions of sodium chloride and calcium chloride; the initial rate of penetration is not the same for both salts, but after

several hours the rates become identical. At the beginning sodium chloride diffuses more rapidly than calcium chloride, the ratio of the two rates being approximately 10:8. Because of the greater adsorption of the cation in the case of calcium chloride the diffusion of ions is hindered to some extent. This occurs at the surface of the colloid, and may help to account for Osterhout's observation of the decrease in permeability when calcium salts are used. When one salt is allowed to penetrate the colloid for a time and then a second salt substituted, the rate of penetration of the ions of the latter seems to be unaffected by the presence of the former. A mixed solution of sodium chloride and calcium chloride gives a curve of fall of resistance similar to that of either of the constituents alone. It approaches in value more nearly the curve of the predominant salt. The ions of sodium chloride and calcium chloride do not antagonise one another as regards their penetration into certain colloidal gels, notably gelatin, and mixtures of gelatin, agar, and whole wheat flour. Determinations of electrical resistance were made of solutions of gelatin to which had been added salts in varying concentrations. The purpose of these determinations was to show whether electrical resistance varies directly with the precipitability of the gelatin as determined by Fenn. The electrical resistance of the gelatin was found to vary directly with the precipitability, which is greatest at the isoelectric point. The isoelectric point occurs when the unadsorbed positive and negative ions of the added salts balance one another. It is assumed that balanced solutions owe their effectiveness to the fact that the protoplasm adsorbs from them equal numbers of positive and negative ions, thus bringing the condition to the isoelectric point, at which there is greatest ionisation of the protein, greatest amount of precipitation, and greatest (or normal) permeability.

CHEMICAL ABSTRACTS.

**The Influence of Electrolytes on the Electrification and the Rate of Diffusion of Water through Collodion Membranes.** JACQUES LOEB (*J. Gen. Physiol.*, 1919, 1, 717—745).—The rate of diffusion of water through a collodion membrane separating the pure solvent from a solution depends on two kinds of forces. First, those of gas pressure which are clearly recognisable in the case of solutions of non-conductors, and secondly, electrical forces which become predominant in the case of low concentrations of solutions of electrolytes. In the diffusion of water through a collodion membrane into a solution of an electrolyte the water molecules are either positively or negatively charged according to the nature of the electrolyte in solution, and these charges are a factor in the rate of diffusion.

Solutions of neutral salts possessing a univalent or bivalent cation influence the rate of diffusion of water through a collodion membrane as if the water particles were charged positively, and were attracted by the anion and repelled by the cation of the electrolyte. The same rule applies to solutions of alkali. Solutions of neutral or acid salts possessing a trivalent or quadrivalent cation

influence the rate of diffusion as if the particles of water were charged negatively, and solutions of acids obey the same rule.

It is experimentally shown that the assumption of a difference in sign of the charge of water molecules (according to the two rules just mentioned) explains all the phenomena that can be observed.

A method is given by which the strength of the attractive electric force of electrolytes on the molecules of water can be roughly estimated and the results of these measurements are in agreement with the two rules. The electric attraction of water molecules by electrolytes increases with an increase in the concentration of the electrolyte, but more rapidly at low concentration than at high concentrations. A tentative explanation for this phenomenon is offered. The rate of diffusion of an electrolyte from a solution to pure solvent through a collodion membrane seems to obey largely the kinetic theory.

J. C. D.

**Colloid Chemistry of Congo Rubin. Theory of Indicators and the Theory of the Colour Change of Organic Substances.**

WOLFGANG OSTWALD (*Koll. Chem. Beihefte*, 1919, 10, 179—288. Compare this vol., ii, 187).—A long theoretical discussion, together with some experimental data, from which it is shown that in the exceptional case of congo rubin variations in the degree of dispersity play the main part in the variations of colour during neutralisation of an acid solution by alkali. It is not to be expected that among the numerous organic colour substances congo rubin alone shows this peculiarity. Consequently, the author still maintains the correctness of his statement (*A.*, 1912, ii, 439) on the basis of the present and previous results. This statement is reiterated in the form: "In the colour change of organic substances, such as indicators, colloid and, in general, dispersoid chemical processes play an important part and in many the controlling part."

J. F. S.

**Quinone-phenolate Theory of Indicators. A Spectrophotometric Method for Measuring the Concentrations of the Quinoidal and Lactoidal Salts and the Equilibrium and Affinity Constants of the Phenolphthaleins and Phenolsulphonphthaleins.**

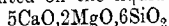
R. T. BIRGE and S. F. ACREE (*J. Amer. Chem. Soc.*, 1919, 41, 1031—1050).—Equations are deduced expressing the relationship between the specific absorption index, the specific colour intensity, and the percentage of intensity of coloured quinone-phenolate salt respectively with the equilibrium and affinity constants of the two acid groups of phenolphthalein and phenolsulphonphthalein indicators. A spectrophotometric method is proposed for measuring the concentration of the monobasic, yellow quinone phenol salt and of the dibasic intensely coloured quinone-phenolate salt in any solution, and the percentage of any indicator transformed into the quinone-phenolate salt in alkaline solution. By the use of the equations developed and the experimental data of Howe and Gibson (*Phys. Rev.*, 1918, 10, 767) and of the authors it is shown that sulphonphthalein indicators are

transformed, practically completely, into quinone-phenolate salts, and are therefore very fine, intensely coloured indicators. Phenolphthalein is changed to the extent of only about 44% into the intensely coloured quinone-phenolate salt, the remainder forming the colourless lactoidal and hydrated salts. Tetrachloro-, tetrabromo-, and tetraiodo-phenolphthalein form only about 1—2% of the intensely coloured quinone-phenolate salt, the remaining 98—99% forming the colourless lactoidal or hydrated salts. These indicators are therefore very poor for analytical work. The introduction of 4 atoms of chlorine into the phthalic acid residue of phenolphthalein makes phenoltetrachlorophthalein an excellent indicator, which changes to the extent of 90% into the intensely coloured quinone-phenolate salt. The introduction of halogens into the phenol groups of phenoltetrachlorophenolphthalein gives bromo- and iodo-derivatives, which can only give 17% and 40% respectively of the highly coloured salt in alkaline solution. The spectrophotometric method used in conjunction with the mass action equations gives an approximate measure of the real equilibrium and affinity constants of the two acid groups of indicators of the phenolphthalein and the phenolsulphonphthalein types. The disappearance of the violet band  $\lambda$  2300 for phenolsulphonphthalein indicates that in alkaline solution the quinone or quinone-phenol group is changed into a quinone-phenolate complex ion like the intensely coloured double compounds made by Jackson (*A.*, 1896, i, 293) by the union of *p*-benzoquinone and phenolates. J. F. S.

**Metastable Unmixing and the Classification of Binary Systems.** F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 1055—1056).—A criticism of Buchner's classification of systems in which, in addition to two liquid phases, compounds also occur, and a consideration of the form assumed by the critical line in three phase systems, when unmixing occurs. J. F. S.

**The Ternary System,  $\text{CaO-MgO-SiO}_2$ .** J. B. FERGUSON and H. E. MERWIN (*Amer. J. Sci.*, 1919, [iv], 48, 81—123).—Cooling curves have been prepared for the ternary system lime, magnesia and silica; the various products have been examined microscopically. The following substances occur as crystalline primary phases: lime; magnesia; silica (tridymite and cristobalite); pseudowollastonite,  $\alpha\text{-CaO.SiO}_2$ ;  $3\text{CaO.2SiO}_2$ ;  $\alpha$ - and  $\beta$ - $2\text{CaO.SiO}_2$ ;  $\text{MgO.SiO}_2$  (clino-enstatite); forsterite,  $2\text{MgO.SiO}_2$ ; diopside,  $\text{CaO.MgO.2SiO}_2$ ;  $5\text{CaO.2MgO.6SiO}_2$ , and  $2\text{CaO.MgO.2SiO}_2$ . The melting point of  $2\text{CaO.MgO.2SiO}_2$  is  $1458^\circ \pm 5^\circ$ , and the decomposition temperature of  $5\text{CaO.2MgO.6SiO}_2$  is  $1365^\circ \pm 5^\circ$ . In addition to these, crystals representing five solid solutions appear as primary phases. These are, (i) a complete series with clino-enstatite and diopside as end members, generally known as pyroxenes; (ii) the pseudowollastonite solid solutions the compositions of which form an area bounded by the following lines: (a) the  $\text{CaO.SiO}_2$ - $\text{CaO.MgO.2SiO}_2$  line; (b) a line running from the composition

$\text{CaO}$ , 44.4;  $\text{MgO}$ , 3.1;  $\text{SiO}_2$ , 52.5, on the above-mentioned line across to the composition  $\text{CaO}$ , 46.7;  $\text{MgO}$ , 3.5;  $\text{SiO}_2$ , 49.8 on the  $\text{CaO}, \text{SiO}_2\text{-}2\text{CaO}, \text{MgO}, 2\text{SiO}_2$  line; (c) then either the last-mentioned line back to  $\text{CaO}, \text{SiO}_2$ , or, more probably, an approximate continuation of line *b* to about the composition  $\text{CaO}$ , 50;  $\text{SiO}_2$ , 50, on the side line. (iii) The wollastonite solid solutions; these extend to about 17% diopside or 3.2% magnesia at the higher temperatures. The most concentrated of these solid solutions along the diopside line (the 17% line) decomposes at  $1340^\circ \pm 5^\circ$ , and this solid solution is the only one represented on the liquidus. (iv) The



solid solutions. Only a few of these solid solutions which are decomposed at the temperatures near the decomposition temperature of the pure compound, are stable in contact with a suitable liquid. (v) Certain members of the monticellite solid solutions. Monticellite takes up forsterite in solid solution to the extent of about 10%, and the decomposition temperature of the solution is thereby raised. Monticellite itself probably decomposes at too low a temperature ever to occur as a primary phase. The temperature-concentration relations of the liquids which may be in equilibrium with each of these phases have been thoroughly investigated by means of the quenching method, and the results obtained have been correlated with the existing data on the remainder of the ternary system. The compounds  $5\text{CaO}, 2\text{MgO}, 6\text{SiO}_2$  and  $2\text{CaO}, \text{MgO}, 2\text{SiO}_2$  have not been prepared previously. Attempts to prepare a compound of the formula  $8\text{CaO}, 4\text{MgO}, 9\text{SiO}_2$  (Schaller's äkermanite) gave negative results. The monticellite solid solutions and the compound äkermanite are discussed at length. Experiments were made on the tridymite-cristobalite inversion temperature, which was found, for this system, to be below  $1500^\circ$ ; this is approximately in agreement with Fenner's original value of  $1470^\circ$ . The great sluggishness of the inversion precluded a more exact determination. J. F. S.

**Critical Solution Temperature of a Ternary Mixture as a Criterion of Purity of Toluene.** KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES (T., 1919, 115, 1055—1070).

**Hydrolysis of some Metallic Acetates.** N. LÖFMAN (*Zeitsch. anorg. Chem.*, 1919, 107, 241—264).—For the determination of the degree of hydrolysis of a large number of metallic acetates use has been made of the method of Westerberg (*Arkiv. Kem. Min. Geol.*, 1917, 6). The method consists in shaking a quantity of ether with successive portions of the acetate solution until equilibrium is reached and estimating the acetic acid content of the ether. The distribution-coefficient of acetic acid between water and ether being known, the degree of hydrolysis of the salt can be calculated. Fresh determinations of this coefficient have been made. For dilutions less than 1:15.N in the aqueous layer it has been found that the distribution-coefficient is independent of the concentration, and for temperatures from  $10^\circ$  to  $25^\circ$  can be expressed by the formula  $k = 1.89 + 0.011t$ . Double molecules of acetic acid are present in the

ether layer. The presence of acetates increases slightly the value of the coefficient, but not enough to affect appreciably the accuracy of hydrolysis determinations of the acetates.

The degree of hydrolysis of the following acetates has been determined: ammonium, sodium, magnesium, aluminium, chromium, manganese, ferrous, ferric, cobalt, nickel, copper, zinc, silver, cadmium, lanthanum, mercury, and lead. In the case of ammonium acetate the hydrolysis was also determined from measurements of the distribution of ammonia between water and air, and by determining the hydrogen-ion concentration of the acetate solution, the results showing very good agreement among themselves and with the theoretical value. The degree of hydrolysis is independent of the concentration except with ferric and aluminium acetates, the abnormal behaviour of which is attributed to the formation of colloidal hydroxides.

E. H. R.

**Quantitative Measurements of the Fission of Hexamethylenetetramine.** PAUL TRENDLENBURG (*Biochem. Zeitsch.*, 1919, **95**, 146—163).—The rate of fission of hexamethylenetetramine into formaldehyde and ammonia is greatly increased at high concentrations of hydrogen ion. Thus, it is completely hydrolysed by treatment with 0.1*N*-hydrochloric acid for six hours at 38°. With decreasing hydrogen-ion concentration the rate of decomposition falls, but not proportionally, being slightly slower. In neutral solutions about 1% of the hexamethylenetetramine is hydrolysed on being kept at 38° for six hours. A negative result is only obtained when the solution is distinctly alkaline. From these results it follows that this substance is decomposed to no inconsiderable extent in the stomach. Even slight decomposition probably occurs in the mild alkalinity of the intestinal contents or body fluids. The value of the base as a means of disinfecting the bladder contents depends on the reaction of the urine.

J. C. D.

**Active Substance in the Iodination of Phenols.** VICTOR COFMAN (*T.*, 1919, **115**, 1040—1049).

**Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium.** EDWARD BRADFORD MANTED (*T.*, 1919, **115**, 1050—1055).

**Catalytic Actions at Solid Surfaces. I. Hydrogenation of Unsaturated Fats in the Liquid State in Presence of Nickel.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 137—146).—Experiments on the rate of hydrogenation of a number of unsaturated fatty oils in presence of finely disseminated nickel have revealed a close analogy between this reaction and the hydrolysis of glucosides in presence of enzymes. The experiments were made with olive oil, cotton-seed oil, whale oil, and linseed oil at about 180°, the rate of hydrogenation being determined by measuring the volume of hydrogen entering and leaving the system by means of water meters. The time-absorption curves,



except in the case of olive oil, are all characterised by an initial linear segment, followed by an abrupt change of direction to a segment of gentler slope, also linear at first but subsequently more or less curved. The position of the point of inflexion of these curves gives the clue to their interpretation. The inflexion takes place on each curve, approximately, at a point when only 10–20% of the glycerides present is derived from acids less saturated than olein. In the case of olive oil this point is reached very soon after the start, and so is difficult to identify on the curve. The curves never approach the logarithmic type required for a unimolecular reaction. The two linear portions represent (1) the hydrogenation of glycerides less saturated than olein, and (2) the hydrogenation of olein itself. Since they are linear they must represent a change in which the acting mass is constant, and, after a reasoned consideration of the possibilities, it is concluded that it is the action of the catalyst that is represented, and, moreover, that the formation of an unstable complex between the nickel and the unsaturated compound must be involved in the reaction.

It has been shown by H. E. Armstrong and others (A., 1913, i, 781) that the hydrolysis of carbamide by urease, and probably most other enzymic reactions, take place at a linear rate, when allowance has been made for the influence of the products of change. The hydrogenation curves show a general resemblance to those obtained in the case of enzymes, and the mechanism of the reaction is probably similar in the two cases, involving the formation and subsequent decomposition of an unstable compound. In each case the interchanges take place in an electrolytic circuit in which the interacting substances and the catalyst or enzyme are all comprised. The action takes place entirely at the surface of minute particles, and the activity of the catalyst depends entirely on the production of the maximum surface and the avoidance of impurities likely to destroy or dirty this surface.

E. H. R.

**Catalysis. VI. Temperature-coefficients of Heterogeneous Reactions.** NILRATAN DHAR (*Proc. R. Akad. Wetensch. Amsterdam*, 1919, 21, 1042–1047. Compare T., 1917, 111, 707).

—A theoretical paper in which it is shown that it is impossible to establish a relation between the order of a reaction and its temperature-coefficient in heterogeneous systems. The temperature-coefficients of catalysed and non-catalysed reactions are also considered.

J. F. S.

**Neutral Salt Catalysis [Corrections].** HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1919, 41, 1092).—A correction of a previous paper under the same title (compare A., 1918, ii, 436). The following corrections are made: p. 1463, the equation  $\text{H}_2\text{O}_2 + \text{IO}' = \text{H}_2\text{O} + \text{I}' + \text{O}_2$  instead of  $\text{H}_2\text{O}_2 + \text{IO}' = \text{H}_2\text{O} + \text{IO}_2'$ ; p. 1477,  $E_1 - E_1$  instead of  $E_1 + E_1$ ; p. 1478, in table VII all figures in the column  $E_1$  should be positive instead of negative, and the column  $E_1 + E_1$  should be  $E_1 - E_1$ ; and on p. 1479 in table VIII in the column  $K \times 10^2/a$ , 14.14 should be substituted for 13.14.

J. F. S.

**Elements in the Order of their Atomic Weight.** RAYMOND SZYMANOWITZ (*Chem. News*, 1919, 119, 58—59. Compare A., 1918, ii, 436).—A further discussion on the atomic weights of the elements based on the condensation theory of their formation.

J. F. S.

**The Position of the Electron Orbits in the Atom and the Periodic System of the Elements.** P. EHRENFEST (*Chem. Weekblad*, 1919, 16, 1037—1044).—A lecture delivered before the Nederlandsche Chemische Vereeniging in Maastricht. W. S. M.

**Mathematical Investigation of the Stability of A. W. Stewart's Atom.** LEONARD C. JACKSON (*Phil. Mag.*, 1919, [vi], 38, 256—266).—A mathematical paper in which the stability of the atom as conceived by Stewart (A., 1918, ii, 395) is considered. The conditions for the equilibrium and stability of the atom are obtained, and they are applied to several special cases for the helium, lithium, and glucinum atoms. It is found that, in each case tried, equilibrium cannot be maintained indefinitely for the inner ring of negative electrons, even in the entire absence of external perturbing forces. Thus, on the atomic theory considered, instability is placed to the account of those elements which are found to be the least stable in reality. The second alternative put forward by Stewart has not been investigated mathematically, and in view of the fact that the Stewart atom explains physico-chemical facts so well, the author points out that some such alternative suggestion may be reasonably expected to give an atom which is more amenable to ordinary dynamics and more successful in explaining physical phenomena. J. F. S.

**Structure of the Atomic Nucleus and its Tendency to Disintegrate.** W. KOSSEL (*Physikal. Zeitsch.*, 1919, 20, 265—269).—A theoretical paper in which the view is advanced that elements of even atomic number up to the value 20 are composed entirely of helium nuclei; beyond this point, the atomic weights indicate the possibility of mixtures. Various cases are considered where  $\alpha$ - and  $\beta$ -disintegrations may occur. The author introduces a function  $z$  which depends on the atomic weight, and is represented by  $z = A/2 - N$ , where  $A$  is the atomic weight and  $N$  the atomic number. The value of  $z$  is plotted against the atomic weight, and the curve thus obtained shown to be practically horizontal up to atomic weight 40, and then it rises in practically a linear manner.

J. F. S.

**Constitution and Structure of an Atom of Nitrogen.** HAWKSWORTH COLLINS (*Chem. News*, 1919, 119, 29—30).—A theoretical paper in which it is suggested that the nitrogen atom is made up of two hydrogen atoms and one carbon atom. This result is reached from a consideration of the theoretical and experimental

results of Rutherford, J. J. Thomson, and Collie and Patterson, and from a consideration of the relative volumes of the atoms. Thus, the relative volume of an atom of carbon at  $15^\circ$  in all carbon compounds in which the element is united to other elements by single bonds is 0.71. The relative volume of an atom of hydrogen at  $15^\circ$  when united to an atom of carbon in the "first position" is always 15.25. The relative volume of an atom of hydrogen at  $15^\circ$  when united to an atom of carbon in the "fourth position" is always 5.76. The relative volume of an atom of nitrogen at  $15^\circ$  when united by single bonds to other elements is 0.71. The relative volume of an atom of nitrogen at  $15^\circ$  when united to a carbon atom by three valencies is  $15.96 = 0.71 + 15.25$ . The relative volume of an atom of nitrogen at  $15^\circ$  in nitrates and nitrites is  $21.72 = 0.71 + 15.25 + 5.76$ . The above results show that the two hydrogen constituents of nitrogen are capable of being expanded from negligible volume to 15.25 and 5.76 respectively.

J. F. S.

**Characteristic Ultra-red Frequencies of Diatomic Bohr Gas Molecules and the Specific Heat at High Temperatures.**

GERDA LASKI (*Physikal. Zeitsch.*, 1919, 20, 269—274).—A mathematical paper in which it is shown that, in the sense of Bohr's theory, the molecular model of nitrogen consists of two positive nuclei of charge  $7e$  separated  $9.1 \times 10^{-9}$  cm. from each other. Near each nucleus are two rings, an inner ring of very small radius containing two electrons, and an outer, bivalent ring of radius  $8.05 \times 10^{-9}$  cm. containing ten electrons. The plane of the outer ring cuts the molecule symmetrically in two. This molecular model corresponds with an atomic model in which a univalent inner ring of two electrons encircles a nucleus, and concentric with this there is a bivalent outer ring of five electrons. The oxygen molecular model consists of two nuclei of charge  $8e$ , two inner rings each containing two electrons and an outer bivalent ring of twelve electrons. The oxygen atom model consists of an inner univalent ring of two electrons and a bivalent outer ring of six electrons.

J. F. S.

**Distribution of Two Kinds of Atoms in the Regular Frankenheim-Bravais Space Lattices.**

G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 190—234; from *Chem. Zentr.*, 1919, i, 781—782).—Experiments on the reaction limits of mixed crystals show that the distribution of two kinds of atoms in a stable complex cannot occur irregularly in accordance with the laws of probability. In the formation of mixed crystals, a distribution occurs with the help of diffusion. After slow cooling of a mixed crystal in which the orderly arrangement of the different atoms has taken place at a higher temperature, a very regular distribution without appreciable variation can permanently persist, as is shown by the fact that the reaction limits are not displaced in the direction of greater concentration of the less active atom

after weeks or months. The crystalline form of well-defined mixed crystals does not differ from that of their components. In similar directions, the properties of mixed crystals are generally as equivalent to one another as in unmixed crystals. Exceptions are found to this rule, however, since in many cases double refraction as been observed in mixed crystals the components of which crystallise in the regular system. The distribution of the atoms is not definitely determined by the postulate of equivalent directions, but becomes definite when the conception of intimate admixture (which occurs at the temperature of rapid diffusion of the atoms) is also introduced. The requirement may be summarised in the statement that accumulations of similar atoms do not occur on the perpendiculars and that the number of lattice perpendiculars of a group is at a minimum. This type of distribution of atom is termed "normal." Two other types of distribution are of interest: (1) such as fulfil the requirements of symmetry but not of most intimate mixture, and (2) those which, whilst having intimate mixture, possess a degree of symmetry lower than that required by the type of lattice. The normal type is the most stable, since, in it, only transitory local changes can be caused by diffusion. Mixed crystals of the third type cannot be optically distinguished from normal crystals into which they should be transformed by rise in temperature. Frankenheim and Bravais have distinguished three types of regular space lattices; the cube, the corners of which are occupied by atoms, is the lattice element of the first, the 8-point lattice. If an atom is considered to be placed in the centre of the cube, the 9-point lattice is obtained, whilst the 14-point lattice is derived by the introduction of atoms at the centres of the faces of the cube in the 8-point lattice. There are two possible ways of determining the normal distribution in these lattices. Either one can choose the corresponding groups in certain directions from the series of groups of lattice perpendiculars, the similar groupings round which are prescribed by the requisite relationships of mixture, or one can dissect the lattices into component lattices. The latter method has marked advantages, but the mixture relationships are thereby definitely fixed. The distribution of the atoms in the various lattices is discussed. The reaction limits of mixed crystals have been studied in such series which have a normal arrangement of atoms. The solubility of hydrogen in palladium, and the limit of this solubility, indicates an instance in which the agent penetrates the lattice; an atomistic explanation of this limit is given on the assumption of a 14-point lattice. In the cases of series of mixed crystals of gold with copper or silver, the reagents do not penetrate the mixed crystals. The atomistic constitution is very closely connected with the different action limits. The differing action limits of different reagents which, for example, withdraw the copper from the mixed crystal, are explained on the assumption that the agents require differing numbers of copper atoms for their action which are only to be found in differing directions. II. W.

**Valency Isomerism.** J. V. DUBSKY (*Chem. Weekblad*, 1919, 16, 984—995).—A summary and discussion of some recently investigated cases of valency isomerism. W. S. M.

**Physical Nature of Valency.** W. KOSSEL (*Naturwiss.*, 1919, 7, 339—345, 360—366; from *Chem. Zentr.*, 1919, iii, 83—86).—The behaviour of carbon in exhibiting a constant valency, previously considered as particularly simple and typical, must be regarded as exceptional when compared with the majority of elements in which the polar character is marked. In general, a distinction must be made between heteropolar and homopolar linkings. The former not only occur more commonly, but also correspond with the best defined characteristics of valency. The double molecules of elementary gases may be regarded as examples of the latter, and in this connexion the polar neutrality of carbon appears exceptional. The position of carbon among the elements indicates its quadrivalency, but this should be positive from analogy with the preceding elements and negative as judged from its successors. Also, the maximum co-ordination number of carbon and its neighbours is four. A certain stability is thereby caused which is not generally associated with homopolar character, and since similar external conditions are only otherwise associated with silicon (and even then not in the same degree), carbon occupies an almost unique position, which, though rendering it able to form an exceptional number of compounds, makes it quite unsuitable for a general study of valency. The electro-chemical valency theory of Berzelius has been repressed, not only by reason of the preponderating developments of the chemistry of carbon, but also by the apparent necessity of attributing an opposite charge to the two similar portions of a molecule, such as that of hydrogen; this difficulty is removed by the conception of electrons. The electric forces need no longer be regarded as proceeding from the atom as a whole. The individual components exercise attractive force towards one another, and may thus cause the union of atoms without leaving the latter and causing them to be discharged, or certain components, symmetrically arranged, may form a uniting bridge between the atoms. The gradual transition from this type of union to that in which the atoms appear as polar (in which the components have passed from one atom to another and the atom as a whole may be regarded as discharged) is perfectly natural. Bohr's hydrogen model represents the most complete representation of a homopolar molecule. The author gives a historical review of the attempts made since the introduction of the conception of electrons to represent atomic structure and valency with the aid of the quantum theory, and discusses the models of Stark, J. J. Thomson, and Rutherford, together with Bohr's modification of the latter. Since the latter assumes that the electrons of an atom invariably follow their paths in regular order, which is necessary for equilibrium, and since their motion must act externally, as if the charge distributed itself uniformly over the path, the

complete model must appear externally as a symmetrical form, the action of which, after reception or expulsion of electrons, must be governed by the total charge which it has received as a whole. The action of such charges can be calculated with considerable certainty on the assumption that the charges are uniformly distributed, that is, that the resultant charge acts at the centre. A particularly simple electrostatic theory of valency of heteropolar compounds is thus obtained. The process of the union of atoms occurs in two stages, the first consisting in the exchange of electrons, the second in the union of ions. The meaning of the regular course of polar valency activity in the periodic system is discussed. For example, the potassium atom has 19 electrons, which are diminished to 18 when it becomes ionised. With chlorine, on the other hand, the number of electrons is increased from 17 to 18 when the free element becomes ionised. Inactive argon has itself 18 electrons, and this number is also attained by multivalent elements, more distant from argon in the system, in the ionised state. It may be generally stated that the strongly polar elements surrounding the rare gases attain the same number of electrons as the latter when combined. The arrangements of electrons in the rare gases are the most stable, and are the only ones which permit the reception of electrons.

Amongst elements of the type of the rare gases, the common arrangement of electrons occasions repelling forces when the atoms approach one another. On the other hand, alteration in valency is attributed to alteration in the charge of the nucleus, which, in conjunction with the constancy in number of the electrons, imparts a varying total charge to the atoms. The properties of such simple atomic models, having a central charge surrounded by an impenetrable zone, can readily be calculated. Although the atoms, in consequence of integral increase in the total charge, unite in integral ratios, there is nothing in the nature of the model which points to the exercise of special forces in spatially fixed directions, as is indicated by the usual structural formulae. Actually, atoms frequently exhibit combining powers which cannot be classed with the definite valencies; Werner's complex compounds provide the best known example of this type. A number which represents the degree of charge, and which is identical with the number of chief valencies, is peculiar to each atom of a polar compound. A neutral molecule, for example, must contain equal charges of either sign; two such molecules, however, may yield a third neutral molecule with the help of the attractive forces of their disengaged charges of opposite sign. On the other hand, the degree of charge determines the affinity of one atom for another, and the work necessary to separate them. This work governs the frequency of separation (degree of dissociation of the compound), and the power of a substance to yield ions depends, therefore, on the valency of the atoms. Elements, such as gold, which possess high valency and small volume, are particularly adapted to function as nuclei in complex compounds, and this property is common to all elements

which have one or both of these characteristics. This point of view is further illustrated by reference to the hydrogen compounds of the elements at the negative end of the periodic table. The acidity decreases from fluorine through oxygen to nitrogen in proportion as the hydrogen is more firmly united in consequence of increased nuclear charge. Similarly, in the groups of the periodic system, hydrogen should be progressively less firmly retained as the atomic volume of the second element increases; this is the case in the sixth, but not in the seventh, group. Thirdly, every atom should detach hydrogen ions from electrostatically weaker atoms.

Thus the  $\bar{O}$  of water removes hydrogen ions from compounds of those elements which are placed to the right and below it in the periodic classification. On the other hand, the  $\bar{N}$  of  $NH_3$  is more potent than  $\bar{O}$ , and therefore removes hydrogen ions from water to form  $NH^+$  and  $OH^-$ .

The behaviour of elements exhibiting various degrees of oxidation, or, more exactly, the maximum degree of hydroxylation of such oxides, affords further possibilities of application for the theory. Such compounds can decompose in two ways, yielding either hydroxyl or hydrogen ions. If a definite assumption is made with regard to atomic radius, the work involved in the dissociation of such compounds within the periodic system can be exactly calculated. Highly charged ions are too unstable to be found free in aqueous solution. Electrostatic attractive forces are capable of representing the forces of valency with such exactitude that it appears doubtful whether other forces are involved. A complete representation of the atoms is necessary if the forces in polar molecules are to be exactly ascertained and the dissociation tensions and heats are to be calculated, and, more particularly, if the laws governing homopolar compounds are to be investigated. The experimental methods consist in observations of the natural vibrations of the atoms (Röntgen and optical spectra, etc.), and of the forced vibrations of the electrons of the atoms (refraction and dispersion of light, dispersal of Röntgen rays). The complete representation of the forces which determine the valency action of atoms involves, not only electrostatic, but also electromagnetic principles, and, in a subsidiary degree, the action quantum.

H. W.

**Alignment Chart for the Solution of Molecular Weight and Vapour Density Problems.** LESLIE J. HARRIS (*Chem. News*, 1919, 119, 49—51). A chart, on the principle of the slide rule, is described whereby from weight and volume measurements the vapour density or molecular weight of a gas may be directly read.

J. F. S.

**Automatic Extraction Apparatus.** JOSEPH TCHERNIAC (*T.*, 1919, 115, 1090—1092).

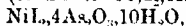
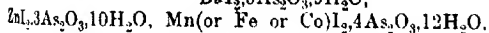
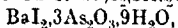
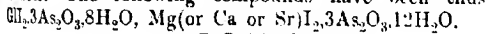
## Inorganic Chemistry.

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**Manufacture of Metal Chlorides.** WILLIAM HEAP and EDGAR NEWBERRY (Brit. Pat., 130626).—The anhydrous chlorides of aluminium, magnesium, cerium, and other rare earths are obtained by treating the oxides, or a salt with a weak acid, such as the carbonate or oxalate, with carbonyl chloride at a suitable temperature. With alumina, a temperature of 350–400° is required; magnesia, 500–600°; and cerium oxide, 650°. The carbonyl chloride may be replaced by a mixture of carbon monoxide and chlorine, passed over a catalyst, such as animal charcoal, before reaching the metallic oxide, and the process may also be used for dehydrating hydrated chlorides of the above-mentioned metals. Although the patent only applies to the above metals, the reaction is general, and is particularly useful also for the preparation of anhydrous calcium and ferric chlorides. G. F. M.

**Preparation of Hydrobromic Acid, using Potassium Bromide, Sulphuric Acid, and Stannous Chloride.** ALWYN TICKLES (*Chem. News*, 1919, 119, 89).—To 25 c.c. of a solution of potassium bromide (90 grams of the salt in 150 c.c. of solution) were added 0.2 gram of stannous chloride and 3.4 c.c. of concentrated sulphuric acid; by distillation at 120–127°, a solution of hydrogen bromide was obtained which was free from tin and almost free from hydrogen chloride, the yield being 95%. If a larger quantity of stannous chloride is used, the distillate contains tin and hydrogen chloride. C. S.

**Compounds of Arsenious Acid with Iodides of Multi-valent Metals.** R. F. WEINLAND and PAUL GRUHL (*Arch. Pharm.*, 1917, 255, 467–481). The iodides of a number of bivalent light and heavy metals, as well as that of aluminium, form compounds with arsenious acid. When the moderately concentrated solution of the iodide, saturated in the hot with arsenious acid, is allowed to cool, the compound, sometimes together with a little free arsenious acid, separates in small crystals, which have no distinct crystalline form, or consist of well-formed, microscopic, hexagonal leaflets. The following compounds have been thus prepared:



$\text{AlI}_3\cdot 6\text{As}_2\text{O}_3\cdot 18(?)\text{H}_2\text{O}$ , and  $\text{LiI}\cdot 2\text{As}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ . In general, the characters of the iodides are suppressed in these compounds, which resemble more the arsenites of the metals. In dry air they are moderately stable, but gradually become yellow or brown, with conversion of the arsenious to arsenic acid in the case of the alkaline earth compounds and oxidation of the metal with



the ferrous and manganous compounds; this decomposition is most rapid with the ferrous, manganous, and aluminium compounds, and may be accelerated by heating the compounds in the air. In a vacuum over sulphuric acid or in a current of hydrogen at  $100^{\circ}$ , the water of crystallisation is completely lost with only minimal decomposition of the compounds; part of the water is reabsorbed from the air. The cobalt salt is pale red, the nickel salt pale green, and the rest colourless. With the exception of that of magnesium, these compounds are sparingly soluble in water, and when heated with water they appear to undergo partial dissociation into the iodides and arsenious acid. When the solutions are evaporated, salts richer in arsenious acid, but of no simple formula, separate out, owing to the fact that the iodide is not in excess as it is in the solutions from which the compounds are originally deposited.

The constitution of the compounds is discussed, and the conclusion is drawn that the anion is formed by union of the molecules of arsenious anhydride with the iodine atom or atoms, whilst the metal forms the cation.

Solutions of chromic and stannous hydroxides in hydriodic acid take up arsenious anhydride, but complete decomposition occurs on evaporation.

Compounds of antimony trioxide similar to the above were unobtainable in aqueous solution, but this oxide dissolves in fused potassium iodide, giving the amber-yellow, transparent, crystalline compound,  $8\text{Sb}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 2\text{KI}$ .

Arsenic trisulphide is insoluble in potassium iodide solution, even on boiling, and solutions of thioarsenites in potassium iodide solution fail to give arsenic trisulphide compounds analogous to those of arsenious anhydride.

T. H. P.

**Freezing of Silicic Acid Coagula and the Problem of the Hydrates of Silica. I. and II.** B. L. VANZETTI (*Atti R. Ist. Veneto Sci.*, 1915—1916, **75**, 261—266; 1916—1917, **76**, 287—292).—The author describes results of experiments following up the work of G. Bruni (*Rend. soc. chim. Rom.*, 1905, **3**, 2) on the comparison of the dehydration of silicic acid gels by evaporation and freezing. It is found that with gels varying in initial concentration from 3 to 10% of silica frozen at about  $-20^{\circ}$ , the final ratio of water to silica depends principally on the initial concentration being higher the more water was initially present. Substantially the same conditions were reached for dehydration by freezing at  $-17^{\circ}$  as for drying in air at constant temperature and humidity. A marked influence in the age of the gels was observed, similar to that noted by van Bemmelen, in that with older gels freezing produced a much more advanced dehydration. The results are regarded as in agreement with the absorption theory and as giving no support to the view that specific hydrates of silica are concerned.

In the second paper further experiments are detailed in which

both the time of drying was greatly prolonged at normal temperature ( $15^{\circ}$ ) and the degree of cooling greatly increased for the freezing experiments, mixtures of carbon dioxide and acetone, and liquid air being used. The results confirm the previous ones for shorter periods and higher temperatures. As before, it was found that the final composition depends entirely on the initial concentration and the age of the gel, and not at all on the temperature of freezing. This independence of the gel state of temperatures down to  $-200^{\circ}$  is regarded as contributing a new datum to the granular theory of the gel constitution. Whilst the status of the last traces of water not removed by freezing cannot yet be decided, the results illustrate the relationship of silicon and carbon and their relative positions in Mendeléev's system; in both cases, in the process of evaporation of water, there is manifest a tendency to the separation of the anhydride passing to conditions of maximal stability, in the one case as solid, in the other as gas.

## CHEMICAL ABSTRACTS.

**Selective Combustion of Carbon Monoxide in Hydrogen.**

ERIC KEIGHTLEY RIDEAL (T., 1919, 115, 993—1006).

**Sodium Hypochlorite.** MALCOLM PERCIVAL APPLEBEY (T., 1919, 115, 1106—1109).

**Action of Copper on Sodium Nitrite.** WALTER PETERS (*Zeitsch. anorg. Chem.*, 1919, 107, 313—316).—Experiments are described in which metallic copper was warmed at  $60^{\circ}$  with a 5% aqueous solution of sodium nitrite, in presence of carbon dioxide, it being excluded from the reaction vessel. Decomposition of the nitrite occurred with evolution of nitrous gases. Analysis of the gas and of the residual solution showed that the former contained nitrous and nitric oxides whilst the latter contained nitrate. The decomposition of the nitrite is not catalytic, but chemical, involving simultaneous oxidation and reduction. It has not been found possible to represent the reaction by an equation. Other metals, such as lead, iron (filings), and cobalt dissolve in the nitrite solution, but without evolution of gas. In the case of cobalt, sodium manganite is formed in solution.

E. H. R.

**Manufacture of Strontium Peroxide.** JAMES BUCHANAN PIERCE, jun. (Brit. Pat., 130840).—Strontium oxide combines directly with oxygen under a pressure of 105—126 kilos. per sq. cm. at a temperature of  $400^{\circ}$ — $500^{\circ}$ . The resulting peroxide contains over 85% of  $\text{SrO}_2$ , and resembles barium peroxide in physical properties.

G. F. M.

**Anhydrous Phosphates, Arsenates, and Vanadates of Lead.** M. ANADORI (*Atti R. Ist. Veneto Sci.*, 1916—1917, 76, 419—433).—Thermal studies of the systems  $\text{PbO}-\text{P}_2\text{O}_5$ ,  $\text{PbO}-\text{As}_2\text{O}_5$ , and  $\text{PbO}-\text{V}_2\text{O}_5$  are described. The investigation was suggested by the analogy of these compounds to the calcium derivatives as in Thomas and in the work of Kroll. Formation of compounds with lead

oxide occurs in the diminishing order  $P_2O_5$ ,  $As_2O_5$ , and  $V_2O_5$ . The PbO content is upwards of 66.66% mol. The phosphates, arsenates, and vanadates are pyro- (as  $P_2O_5 \cdot 2PbO$ ), ortho- (as  $P_2O_5 \cdot 3PbO$ ), and octa- (as  $P_2O_5 \cdot 8PbO$ ). In addition, there is an anorthophosphate,  $2P_2O_5 \cdot 5PbO$ , and a metaphosphate,  $P_2O_5 \cdot PbO$ . A tetraarsenate,  $As_2O_5 \cdot 4PbO$ , is probably also formed.

CHEMICAL ABSTRACTS.

**Thallium-Tin Alloys.** PAUL FUCHS (*Zeitsch. anorg. Chem.*, 1919, 107, 308—312).—A thermal investigation of the alloys of thallium and tin has shown the existence of a eutectic point at  $166^\circ$  with 30 at. per cent. of thallium. The eutectic horizontal extends from 0 to 73 at. per cent. of thallium; with a greater proportion of thallium the alloy forms homogeneous, mixed crystals. Alloys with less than 73% of thallium show on cooling, in addition to the arrest point at the eutectic temperature, a second arrest at  $144.5^\circ$ . This arrest point represents the transition point of thallium, lowered through the influence of the tin from about  $231^\circ$ , the transition point of pure thallium. In the mixed crystal region, that is, from 73 to 100% of thallium, the transition point is lowered approximately in proportion to the amount of tin present. The arrest point at  $144.5^\circ$  is the transition point of saturated mixed crystals containing 73 at. per cent. of thallium. E. H. R.

**Aluminium and a Double Salt.** E. RATTENBURY HODGES (*Chem. News*, 1919, 119, 64).—When aluminium foil is submitted to the action of dilute nitric acid for seven to eight weeks it dissolves, and on evaporating the solution a light grey, colloidal mass containing some free acid is obtained. This solid is nearly all hydroxide, and on exposure to a moist atmosphere is completely converted into hydroxide. J. F. S.

**Ternary Alloys of Aluminium with Magnesium and Copper.** RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1919, 107, 265—307).—A thermal and microscopical study has been made of ternary aluminium-magnesium-copper alloys containing up to 55% of magnesium and 54% of copper, and from the results the solid, triangular equilibrium diagram limited by the phases Al, AlCu, and  $Al_3Mg$ , has been constructed. It is known that, with copper, aluminium forms mixed crystals containing up to 4% of copper, whilst with a greater proportion of copper an eutectic of these mixed crystals and the compound  $Al_2Cu$  is formed. It is now found that aluminium also forms mixed crystals with magnesium with a maximum magnesium content of 6%. With more than this proportion of magnesium a second mixed crystal constituent appears containing the compound  $Al_3Mg_4$ . This constituent being hard and brittle, the presence of more than 6% of magnesium in these alloys is likely to be disadvantageous.

The compositions of the ternary alloys examined were so chosen that seven sections of the Al-Al<sub>2</sub>Cu-Al<sub>3</sub>Mg<sub>4</sub> diagram could be constructed, and from them the complete three dimensional diagram

deduced. These sections and the complete diagram are fully discussed. The following constituents occur in the ternary alloys: ternary mixed crystals of the three elements, ternary mixed crystals containing  $\text{Al}_2\text{Cu}$ , a ternary compound,  $\text{Al}_3\text{Mg}_2\text{Cu}$ , and binary Al-Mg mixed crystals. When a polished section of a ternary alloy is etched with concentrated nitric acid, the mixed crystals containing  $\text{Al}_2\text{Cu}$  are blackened in about half a minute, the crystals of the ternary compound become brown to black much more slowly, the mixed crystals of the series containing more than 6% of magnesium become yellow, whilst the ternary mixed crystals rich in aluminium remain bright. On adding a drop of water to the nitric acid the black  $\text{Al}_2\text{Cu}$  mixed crystals become bright red owing to the deposition of copper, whilst the ternary compound rapidly blackens. A number of photomicrographs of different alloys are reproduced. The ternary compound forms crystals which are hard and brittle; consequently, it is an undesirable constituent.

Binary alloys of aluminium with 1–10% of magnesium show a secondary arrest point at  $584^\circ$ , with 2–5% of copper at  $513$ – $529^\circ$ , and with both magnesium and copper present, between  $557^\circ$  and  $564^\circ$ . It appears probable that this thermal effect is due to an allotropic change of the aluminium induced or accelerated by the foreign constituent. The aluminium used contained some iron and silicon, but no microscopic evidence of the formation of an eutectic with either of these elements could be detected. A similar arrest point was observed by Gwyer (A., 1908, ii, 284) with aluminium alloys containing nickel and cobalt. The possibility of allotropic change of the aluminium does not explain, however, the increase in tensile strength which aluminium alloys containing magnesium and copper undergo after heating to about  $500^\circ$  and cooling to the ordinary temperature. This phenomenon cannot yet be explained.

E. H. R.

#### Regularities in the Chemical Action of Gases on Iron and its Compounds with Non-metals at High Temperatures.

FRIEDRICH SCHMITZ (*Stahl u. Eisen*, 1919, **39**, 373–381, 406–413; from *Chem. Zentr.*, 1919, iii, 6–7).—When pure hydrogen is passed over strongly heated technical iron or is blown through molten iron (pig iron, ferrous alloys, steel), the non-metals which are present in the free or combined state are converted into the corresponding gaseous hydrides; the behaviour of pure non-metals (carbon, silicon, arsenic) is similar. The hydrides dissociate to some extent at the high temperature, and the nascent hydrogen, in the absence of oxygen, can reduce silica, even at  $700^\circ$ , to silicon hydride. The salts of iron are converted at elevated temperature in the presence of hydrogen into iron and free acids. If, on the other hand, iron is ignited in a gaseous hydride, hydrogen is liberated, which, in part, diffuses into the iron, and the non-metal or acid radicle combines with the iron. Under definite external conditions of temperature and pressure, an equilibrium is set up for each non-metal; a definite relationship between hydrogen and non-metallic hydride is established, at which neither cementation nor

tempering occurs. In an atmosphere of pure hydrogen or nitrogen at an elevated temperature, both carbon and silicon can diffuse into solid iron without previous formation of gaseous substances.

Compounds of iron, oxygen, and the corresponding non-metal are formed when metalloid compounds of iron are ignited in pure oxygen. If these compounds contain carbon, sulphur, or arsenic, they decompose at a higher temperature, yielding ferric or ferrous oxide and the gaseous oxide of the metalloid. If iron is ignited in a gaseous compound of a metalloid, which can be replaced by hydrogen, and oxygen, a compound of iron, oxygen, and the non-metal or hydrogen is first produced. Such compounds, which contain phosphorus and silicon, are stable when the temperature is raised; those, however, in which carbon, sulphur, arsenic, and hydrogen are present decompose at a slightly increased temperature, giving ferric or ferrous oxide and gaseous compounds of the non-metal or hydrogen with oxygen. Nitrogen has no action on non-metals present in solid or liquid iron. The diminution in the carbon content, frequently observed after ignition in nitrogen, becomes progressively smaller as greater care is taken to free the nitrogen from oxygen and gases containing oxygen. H. W.

#### **Alloys of Iron and Nickel Deposited Electrolytically.**

P. BENVENUTI (*Atti R. Ist. Veneto Sci.*, 1916, **76**, 453—477).—The author reviews the work of Bruni and Amadori and other experimenters in depositing alloys containing nickel and iron, and describes his own investigations to discover the best conditions for producing the deposit. The composition of the bath and its relation to the composition of the alloy deposited is discussed from his data. The physical structure of Ni-Fe alloys of different composition is shown in photomicrographs. Tables show the atomic % of iron varying from 2 to 97, the duration of the electrolysis, the weight of the alloy deposited, and the weight and % of the iron contained in the deposit. Iron in the alloy was estimated volumetrically by permanganate. The cell was maintained at 25° ( $\pm 0.1^\circ$ ) in a thermostat and platinum electrodes were used. Each electrolysis lasted about eight hours. Current was maintained at 25 milliamp. and the current density at the cathode was 0.5 ampere per sq. dm. The two metals may be easily deposited simultaneously. An ammonium tartrate bath with less than 73% or more than 75% of iron gives deposits containing more and less iron respectively than is contained in the solutions. A bath containing 26% of nickel and 74% of iron deposits an alloy of the same composition, which is that of stable equilibrium at ordinary temperature and pressure, and is also that of the eutectic alloy, and that of the solid saturated solution, the meteoric mineral tennite, solid solution of iron in nickel, and of kamazite, solid solution of nickel in iron. The deposits by the current are such as to indicate in the deposits the co-existence of two types of saturated solid solution. The study of the electrolytic potential supports the hypothesis proposed above. The micrographic study of the deposits furnishes evidence of the presence of two structures in all the alloys, what-

ever may be their composition. It is probable that in the course of their deposition, the alloys Fe-Ni electrolytically tend, without reuniting, towards the state of equilibrium of nickeliferous iron in the original meteorites.

CHEMICAL ABSTRACTS.

**Meteoric Nickel-Iron and the Polymorphism of Carbon-iron.** G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 258—266; from *Chem. Zentr.*, 1919, i, 806—807).—According to Osmond and Cortaud (*A.*, 1904, ii, 135), ténite is to be regarded as a particular phase, since it is sharply separated from kamacite, particularly after being etched. The author, however, is more inclined to regard it as a deposit in kamacite rather than to consider that the substances represent two phases in equilibrium with one another. According to the recent experiences on the reaction limits of chemical agents on mixed crystals, two portions of a conglomerate which show widely differing behaviour towards reagents are not necessarily to be regarded as distinct phases. The determination of limits of action in technical nickel-iron is rendered impossible by the presence of oxygen. It appears questionable whether ténite itself is homogeneous. If the latter is not regarded as a separate phase, there is no difficulty in interpreting the meteoric structure on the basis of the known equilibrium diagrams of nickel steels, and the meteoric structure may be assumed to be due to the crystallisation of the respective molten masses. In this case there must not be expected the normal, stable distribution of the nickel and iron atoms, such as occurs in the space lattice of technically homogenised nickel irons, but a different, unstable arrangement. The structure of meteoric iron shows the manner in which the distribution of both kinds of atoms in kamacite differs from the normal. The atoms of the meteorite, like those of technical nickel-iron, probably occupy the points of a 14-point space lattice, the element of which is the cube with atoms at the corners and in the middle of the sides; the latter occupy the corners of an inscribed octahedron. The difference between kamacite and technical nickel-iron may be explained by assuming that, in the former, the lattice perpendiculars parallel to the edges of the octahedron are occupied by an abnormal number of nickel atoms. It is admitted that a form which is unstable when heated may be permanent when it has separated from the molten state. According to the author, therefore, kamacite is a mixed crystal in which the distribution of the nickel and iron atoms is not normal, but of lower symmetry, similar to the mixed crystals with double refraction. The ténite leaflets are layers orientated on the octahedral planes, whilst plessite represents portions richer in layers. Unstable forms, which are probably to be regarded as space lattice isomerides, are also found in carbon steels.

H. W.

**Monoclinic Double Selenates of the Cobalt Group.**

A. E. H. TUTTON (*Proc. Roy. Soc.*, 1919, [A], 96, 156—184).—Continuing the crystallographic investigation of the salts

of the series  $R_2M(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ , the author now reports the results of the examination of the four salts in which M is cobalt and R is potassium, rubidium, caesium, and ammonium. As in the case of the corresponding double ferrous selenates (this vol., ii, 346), all four salts crystallise in the holohedral class of the monoclinic system and are isomorphous with the other members of the series. The relations between the four salts correspond exactly with those found in the case of the salts of the ferrous group.

Potassium cobalt selenate,  $\text{K}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $a:b:c=0.7522$ :  
1:0.5062,  $\beta=104^\circ 17'$ ,  $D_x^{20}$  2.530, M.V. 208.6.

Rubidium cobalt selenate,  $\text{Rb}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $a:b:c=0.7427$ :  
1:0.5019,  $\beta=105^\circ 14'$ ,  $D_x^{20}$  2.837, M.V. 218.49.

Cæsium cobalt selenate,  $\text{Cs}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $a:b:c=0.7310$ :  
1:0.4989,  $\beta=106^\circ 18'$ ,  $D_x^{20}$  3.094, M.V. 230.73.

Ammonium cobalt selenate,  $(\text{NH}_4)_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $a:b:c=$   
0.7449:1:0.5031,  $\beta=106^\circ 23'$ ,  $D_x^{20}$  2.228, M.V. 218.1.

Comparing the molecular volumes of analogous double sulphates and selenates of the different groups which have been investigated, it is seen that the replacement of one atom of sulphur by one of selenium increases the molecular volume by a quantity varying only between the limits 6.0 to 6.8 units. In the simple alkali sulphates and selenates the increase is 6.5 to 6.8 units per atom substituted. The optical constants of the salts have been accurately determined.

E. H. R.

**Action of Oxygen on the Precipitation of Metals from Cyanide Solutions.** OLIVER P. WATTS (*Chem. Met. Eng.*, 1918, 19, 652—653; from *Chem. Zentr.*, 1919, i, 811).—According to Crowe (*Chem. Met. Eng.*, 1918, 19, 283), the precipitation of gold is caused by hydrogen liberated by the zinc, so that removal of dissolved air from the cyanide solution acts favourably, since it prevents the loss of reducing agent by oxidation. The author, on the other hand, is of opinion that the gold is directly precipitated from its solutions by zinc in the same manner as is copper from copper sulphate solution. The solution of zinc in sodium cyanide only differs from its solution in copper sulphate in that hydrogen is liberated in place of copper. The presence of oxygen is necessary for the rapid solution of zinc or other metals in cyanide solutions, whilst it has no influence on the solution of zinc in copper sulphate. Two simultaneous actions occur when zinc is placed in a dilute solution of cyanide containing gold. A portion of the zinc is dissolved by the double cyanide with precipitation of gold, whilst another portion is dissolved by the sodium cyanide with evolution of hydrogen; only the former action is useful in the separation of gold. For every gram of hydrogen evolved, 32.5 grams of zinc are dissolved without precipitation of gold, whilst, also, the excess of cyanide with which the zinc reacts is not profitably utilised. This undesired solution of zinc is limited by the content of oxygen or air, which oxidises the polarising deposit of hydrogen. Not only does dissolved air cause a loss of zinc, but it also diminishes the

yield by expediting the re-solution of the precipitated gold in the same manner as it promotes the solution of metals in the treatment of ores with cyanide solutions.

H. W.

## Mineralogical Chemistry.

**Theory of Magmatic Mineral-forming Agents.** JOHANN JAKOB (*Zeitsch. anorg. Chem.*, 1919, **106**, 229—267).—An important part in mineral and rock formation has undoubtedly been played by the gaseous and more or less easily volatile substances present in the magma. Among these mineral-forming agents water is by far the most important; other agents discussed include hydrogen sulphide, hydrogen fluoride, the oxides of carbon, sulphur dioxide, titanium dioxide, and a number of the less common metallic and non-metallic oxides. A precise definition of a mineral-forming agent cannot be given, but it must possess the property of forming additive compounds with other substances present in the fluid magma. These compounds are supposed to be of the co-ordinated type and generally to form mobile, complex ions. Through the interaction of these complex ions in the magma the different minerals are formed. For the purpose of discussion, the magma is considered as a highly concentrated solution of the other constituents in the mineral-forming agent; for example, in the case of water, as an aqueous solution. Hydrated forms of the different oxides present are probably produced, in which the elements can be supposed to exert the maximum co-ordinating power, with formation of such compounds as  $[(H_2O)_2Si(OH \cdot OH)_4]H_4$  and  $[Mg(OH)_2(OH_2)_4]$ .

At the high temperature of the magma, water is comparatively highly dissociated, and the hydrogen and hydroxyl ions combine with the hydrated compounds to form complex hydrated ions, through the interaction of which the different minerals are formed. New formulæ of the co-ordinated type are suggested for some of the complex silicates. The same ideas are applied to the discussion of rock metamorphosis.

E. H. R.

**Chemistry of Coal. I. Action of Pyridine on the Coal Substance.** WILLIAM A. BONE and REGINALD J. SARGEANT (*Proc. Roy. Soc.*, 1919, [A], **96**, 119—136).—Experiments on the solvent action of pyridine on coal have shown that the presence of oxygen has an important retarding action, varying with the nature of the coal, on the extraction process. This is due to the oxidation of the coal substance which may occur before or during the extraction. Previous oxygenation of the coal renders it much less susceptible to the solvent action of pyridine. The presence of water in the pyridine also has a retarding influence. To obtain concordant results



it is therefore necessary to exclude air, to use carefully dried and purified pyridine, and in addition to grind the coal to a standard mesh and to have a standard form of extraction apparatus. Such an apparatus is described in the present paper. The picolines extract about the same amount as pyridine, but, owing to their greater instability, they are less suitable as solvents. When the pyridine extract, which may amount to more than 30% by weight of the original coal, is again extracted with chloroform about 50% is dissolved. According to Clarke and Wheeler (T., 1913, 103, 1704), the chloroform effects a complete separation of the resinic from the cellulosic constituents of the coal, but the analysis of the pyridine-chloroform extract does not warrant the view that it represents even an approximately pure coal resin. [See also *J. Soc. Chem. Ind.*, 1919, October.] E. H. R.

**Relations between Tridymite and Cristobalite.** C. N. FENNER (*J. Soc. Glass Tech.*, 1919, 3, 116—125).—The author disputes the conclusion of Rees (*J. Soc. Glass Tech.*, 1918, 2, 253), Scott (*ibid.*, 1918, 2, Abs. 169), and Le Chatelier (A., 1917, ii, 97) that tridymite is more stable than cristobalite at temperatures above 1480°. He cites numerous experiments to the contrary, and states that in the course of a long series of experiments, no obvious loophole was left by which it was possible to escape the conclusions regarding the stability relations which have been drawn. At temperatures above 1470±10°, quartz, tridymite, and amorphous silica have repeatedly and unequivocally been converted into cristobalite; between 1470±10° and 870±10°, quartz, cristobalite, and amorphous silica have similarly been converted into tridymite; and below 870±10° tridymite, cristobalite, and amorphous silica have been converted into quartz. These relations have been confirmed again and again. Moreover, recent work by Ferguson and Merwin (A., 1918, ii, 362) has indicated that the melting point of tridymite is considerably lower than that of cristobalite. It follows necessarily from this observation that cristobalite is the high-temperature form. [See *J. Soc. Chem. Ind.*, 1919, 722A.] A. B. S.

**Composition of Bornite.** AUSTIN F. ROGERS (*Science, New York*, 1915, [N.S.], 42, 386—388).—The formula proposed by Kraus and Goldsberry (A., 1914, ii, 570; compare Allen, A., 1916, ii, 391) is discussed. Fifty-nine published analyses are plotted on a triangular diagram; they all fall near the line  $\text{Cu}_3\text{FeS}_3$  to  $\text{Cu}_2\text{S}$ , with the greatest cluster near  $\text{Cu}_2\text{FeS}_4$ , and lower and upper limits near  $\text{Cu}_3\text{FeS}_3$  and  $\text{Cu}_{12}\text{Fe}_2\text{S}_9$ . The most probable explanation of the variations in composition of bornite is that of a solid solution of  $\text{Cu}_2\text{S}$  in  $\text{Cu}_3\text{FeS}_3$ , the formula being written as  $\text{Cu}_3\text{FeS}_3(\text{Cu}_2\text{S})_x$ . L. J. S.

**Scapolite of Gem Quality from the Pegmatites of Madagascar.** A. LACROIX (*Compt. rend.*, 1919, 169, 261—264).—Transparent, yellow scapolite occurs as corroded and striated square prisms several cm. in length, together with beryl, euxenite, and monazite, in a potash-pegmatite at Tsarasaotra on the Tsibohaina

river. D 2.67. Optically uniaxial and negative with slight pleochroism,  $n_x = 1.5698$ ,  $n_y = 1.5490$ ,  $n_z = 1.5490$ ,  $n_x - n_z = 0.0208$ . It is rather harder (H 6½) than ordinary scapolite and shows no cleavage, the fracture being conchoidal. Estimations of some of the more unusual constituents gave (compare this vol., ii, 163):

| CO <sub>2</sub> . | Cl.  | F.   | SO <sub>3</sub> . | SrO. | FeO. | Fe <sub>2</sub> O <sub>3</sub> . |
|-------------------|------|------|-------------------|------|------|----------------------------------|
| 2.52—2.71         | 1.59 | 0.37 | nil               | 0.09 | 0.90 | 0.11                             |

Cut stones resemble certain beryls in appearance and in some of their characters; there is, however, a marked difference in the strength of the double refraction and in the hardness. L. J. S.

### Analytical Chemistry.

**Normal Temperature for the Standardisation of Chemical Apparatus, etc.** WALTER BLOCK (*Chem. Zeit.*, 1919, 43, 477—479).—The author discusses the subject regarding the temperature at which laboratory apparatus should be standardised, and considers that 20° would be more suitable and convenient than 15°, a temperature now usually taken as the normal in chemistry and physics. W. P. S.

**Automatic Apparatus for Gas Analysis.** OLOF RODHE (*Stensk. Kem. Tidskr.*, 1919, 31, 5—14).—The apparatus automatically estimates and records by means of a kymograph the relative amounts of oxygen, carbon dioxide, carbon monoxide, hydrogen, methane, or other constituent in a gas. It is constructed on the principle of a train of absorption, combustion, and measuring units without taps. One or more aggregates may be used and the flow of gas may be shunted from one to another, depending on the constituent considered significant in the control work, for example, carbon monoxide or hydrogen in a water-gas plant, carbon dioxide or oxygen in a lime or cement kiln, etc.

CHEMICAL ABSTRACTS.

**Gas Burette.** PAUL NICOLARDOT and GUSTAVE PREVOT (*Ann. Phys.*, 1919, 12, 140—145).—The apparatus consists of a graduated tube, about 2 cm. in diameter, the upper part of which is widened out so as to form a cylinder of about 6 cm. in diameter and having a capacity three to four times that of the narrow tube; the wide portion of the burette is also graduated. The two ends of the burette are provided with taps. The capacity of the whole burette may be from 200 to 400 c.c. W. P. S.

**Apparatus for the Collection of Gases in Spring Waters, etc.** O. HACKL (*Chem. Zeit.*, 1919, 43, 421—422).—A wide-mouthed bottle is closed with a rubber stopper through which pass the stem of a funnel and a short length of glass tubing.

To collect gases rising from a natural spring, the bottle is filled by immersing it in the water, then inverted so that the bubbles of gas are collected by the funnel and pass into the bottle, the water leaving the latter through the glass tube. When the bottle is full of gas, the stopper is removed while the bottle is still immersed in the water, and another stopper carrying two tubes is inserted; the outer ends of these tubes are closed by short lengths of rubber tubing carrying pinch-cocks. The gases are transferred to a Hempel apparatus by means of these tubes. A Bunsen collecting tube may also be used for the purpose, the end being closed with a rubber stopper carrying a funnel and side-tube; the stem of the funnel is provided with a length of rubber and glass tubing which extends below a constriction in the collecting tube just below the stopper.

W. P. S.

**The Boiling Point as a Criterion of Purity and a New Apparatus for its Determination without Correction for the Thermometer.** THEODOR PAUL and KARL SCHANTZ (*Arch. Pharm.*, 1919, 257, 87—129).—The methods for the determination of the boiling point prescribed in the fifth edition of the German Pharmacopœia, when required for purposes of identification and as a means of controlling purity, have been critically examined. The latter method (distillation of a measured volume of the liquid under definite conditions) only gives a rough approximation of the true b. p., so that the data recorded in the Pharmacopœia do not generally coincide with the actual b. p.'s of the respective liquids even when these in other respects satisfy the pharmaceutical requirements. Further, the influences of variation in the barometric height and of the projecting thread of the thermometer are not taken into consideration.

The influence of common impurities on the b. p.'s of pharmaceutical preparations has been investigated. Addition of water lowers the b. p. of ethyl ether until it is present to the extent of 1.3%, after which no further depression occurs; ethyl alcohol, on the other hand, raises the b. p. of ethyl ether, and a specimen of the latter containing 1.15% of ethyl alcohol and 1.8% of water (by weight) has the same b. p. as pure ethyl ether. The depression of the b. p. of chloroform by addition of ethyl alcohol has been further studied; water produces a similar effect, but the quantitative relationships could not be studied by reason of peculiar condensation phenomena. The b. p. of ethyl bromide is depressed by the presence of ethyl alcohol or water, the effect of which when simultaneously present is additive. The presence of benzoic acid elevates the b. p. of benzaldehyde.

The boiling points for different barometric pressures, calculated according to the formula  $t = t_0 - (t_0 + 273) \cdot c \cdot (760 - h)$ , agree satisfactorily with the observed values.

A new apparatus is described which allows the determination of the boiling point of a liquid at constant composition and during fractional distillation. The vessel consists of a stout-walled test-tube about 18 cm. high and 20 mm. internal diameter which con-

tains a layer, 3 cm. high, of beads. So much liquid (about 15 c.c.) is used that its surface is about 3.5 cm. above the beads. A column is attached to the test-tube consisting of a vapour tube (23 cm.  $\times$  11 mm.) which is surrounded by a vapour jacket (20—22 cm.  $\times$  20 mm.), in which the thermometer is supported. The jacket and tube are sealed together about 14 cm. above the lower end of the tube. Immediately above the junction, a side-tube, which can be connected with a condenser, and a small bent tube, which is also sealed in to the lower portion of the vapour jacket and permits the condensed liquid to return to the still, are attached. The vessel is placed in the middle of an asbestos sheet in which a hole, 2 cm. in diameter, has been cut, the opening being closed from below by copper gauze. The asbestos sheet must be sufficiently large to prevent the radiant heat from the burner from affecting the thermometer. For liquids which boil above 100°, it is advisable to protect the boiling tube with an air-jacket. The thermometer is inserted in such a manner that the thread is completely surrounded by the vapour. The height of the flame is so adjusted that the liquid just boils vigorously. The b. p. is read when the thermometer does not show a variation greater than one-tenth of a degree during three minutes. By rotating the condenser through 180°, the apparatus may be used either for refluxing or for distillation.

H. W.

**Substitute for Hydrogen Sulphide Water.** RAYER (*Pharm. Post.* 1918, 354; *Schweiz. Apoth. Ztg.*, 1919, 57, 140).—Ten grams of sodium sulphide are dissolved in 50 c.c. of water + 50 c.c. of glycerol. No special apparatus is required.

CHEMICAL ABSTRACTS.

**Stabilising Normal Alkali Solution.** WINKLER (*Pharm. Post.* 1918, 354; *Schweiz. Apoth. Ztg.*, 1919, 57, 140).—The absorption of carbon dioxide by N-alkali may be reduced to a minimum by replacing 30% of the water used by 30% of glycerol. This also prevents the sticking of glass stoppers.

CHEMICAL ABSTRACTS.

**Conditions for Obtaining Pure Sodium Carbonate for Standardising Acid and Applicability of Crystallised Oxalic Acid in place of the Anhydrous Acid as a Titration Standard.** HERMANN KUNZ-KRAUSE and RUDOLF RICHTER (*Arch. Pharm.*, 1917, 255, 540—549).—If stirred with a platinum wire, sodium hydrogen carbonate is converted quantitatively into sodium carbonate at 250°. Microcrystalline oxalic acid (+ 2H<sub>2</sub>O) may be used for the direct preparation of standard acid; its solutions keep their titre if protected from the light. [See *J. Soc. Chem. Ind.*, 1919, October.]

T. H. P.

**Liquid Ammonia-Sodium Method for [Estimating Halogens in Organic Compounds, the Formation of Cyanide and the Method of Removing [it] from the Solution.** CHARLES WILLIAM CLIFFORD (*J. Amer. Chem. Soc.*, 1919, 41, 1061—1060).—This method of estimating halogens in organic com-

pounds, due to Chablay (A., 1914, i, 918), consists in adding liquid ammonia to a small quantity of the substance in a Dewar vessel, and then metallic sodium until a permanent blue colour is produced. The halogen is thereby converted into the sodium haloid. The excess of ammonia is allowed to evaporate, and the excess of sodium is removed by treatment with alcohol. The residue is dissolved in water acidified with nitric acid, treated with excess of standard silver nitrate, and the excess of silver titrated with sodium thiocyanate. This reaction has been investigated as to its trustworthiness. It is found that in many cases cyanide is also formed, and consequently the procedure as outlined above cannot, in many cases, be carried out without the possibility of error. On acidifying, only a portion of the hydrocyanic acid which may have been formed is expelled. At best, the decomposition of silver cyanide and elimination of cyanide by boiling in diluted nitric acid are only approximately quantitative. The percentage of cyanide formed is not a constant for each substance under the conditions of analysis. Treatment with sodium in liquid ammonia completely removes any halogen present in organic compounds, and the resulting haloid is separated quantitatively from any cyanide present by acidifying the solution with acetic acid and boiling. J. F. S.

**Adaptation of the Mohr Volumetric Method to the General Estimation of Chlorine.** LESTER YODER (*J. Ind. Eng. Chem.*, 1919, 11, 755).—The following procedure is recommended for the estimation of chlorine in organic substances. A suitable quantity of the sample is treated with 5 c.c. of 30% calcium acetate solution and sufficient water to form a moist mass, the mixture is evaporated to dryness, and incinerated below 450°. The cooled residue is moistened with a few c.c. of 10% ferric acetate solution, again dried, and ignited below 450°. The residue is dissolved in water, the solution filtered, the filter washed with hot water, the filtrate evaporated to dryness, and this residue dissolved in a small quantity of water. After the addition of a few drops of potassium chromate solution, the chloride is titrated with standardised silver nitrate solution. The calcium acetate fixes free chlorine, precipitates carbonates, and neutralises the filtrate; the ferric acetate precipitates phosphates, and the excess is converted into insoluble ferric oxide during the ignition. W. P. S.

**Simplification of Kjeldahl's Method in Clinical Chemistry.** E. PITTARELLI (*Riv. crit. clin. med.*, 1919; from *J. Pharm. Chem.*, 1919, [vii], 20, 32—34).—To estimate nitrogen in urine, 1 c.c. of a 10% solution of the sample is digested with 2 c.c. of sulphuric acid and one drop of phenol, a small quantity of potassium persulphate being added towards the end of the reaction. The mixture is then neutralised, treated with 10 c.c. of a mixture of three volumes of saturated sodium hydrogen carbonate solution and one volume of saturated mercuric chloride solution, the whole

diluted to 250 c.c., and the turbidity compared with that obtained with a known quantity of ammonia.

W. P. S.

**Systematic Procedure for the Detection of Acids of Group I.** LOUIS J. CURTMAN and DAVID HART (*Chem. News*, 1919, 119, 25—29, 37—40).—A scheme is proposed by means of which the acids of group I may be systematically detected and the relative amounts approximately estimated. The chief steps in the scheme are (a) a preliminary precipitation of all the acids of group I with a mixture of barium and calcium chlorides, (b) treatment of the precipitate with hydrochloric acid to dissolve all but the sulphate, (c) oxidation with hydrogen peroxide to convert sulphite into sulphate and precipitation of the latter with barium chloride, (d) removal of barium from the solution with ammonium sulphate, (e) separation of fluoride, arsenate, and phosphate from borate and tartrate in alkaline solution in the presence of sufficient ammonium salts, (f) removal of oxalate and fluoride from arsenate and phosphate in an acetic acid solution containing an excess of calcium ions, (g) reduction of arsenate to arsenite with sulphur dioxide and separation from phosphate by hydrogen sulphide in hydrochloric acid solution, (h) separate tests for carbonates and chromates, and (i) separate tests for the determination of the state of oxidation of the arsenic. Very full details of the effect of the various acids on one another in the several stages of the separation are given, and by means of these the method is shown to be trustworthy.

J. F. S.

**Influence of Temporary Hardness on the Estimation of Chlorides in Water.** W. HERBIG (*Zeitsch. angew. Chem.*, 1919, 32, 216).—The temporary hardness of water is without influence on the estimation of chlorides by Mohr's method, and consequently the procedure adopted by Lombard (A., 1913, ii, 1068) is unnecessary.

W. P. S.

**Rapid Estimation of Nitric Acid.** LUCIEN MAUGÉ (*L'Ind. chimique*, 1918, 8, 255—256; from *Chem. Zentr.*, 1919, ii, 720).—When nitric acid is added to a solution of ferrous sulphate acidified with sulphuric acid, oxidation of a portion of the salt occurs, accompanied by formation of nitric oxide, which yields the intensely brown additive compound with the excess of ferrous sulphate; on further addition of nitric acid, the colour disappears as soon as the ferrous sulphate is completely oxidised:  $6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 2\text{HNO}_3 = 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 4\text{H}_2\text{O}$ . The discharge of the colour is sufficiently sharp for the process to be applied to the volumetric estimation of nitric acid. The solution of ferrous sulphate contains 66.66 grams  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per litre, and is standardised by permanganate; 10 c.c. of this solution are heated with 50 c.c. of sulphuric acid (60—66 Bé.) and titrated with the nitric acid under investigation until decolorised.

H. W.

**Estimation of Phosphoric Acid as Magnesium Pyrophosphate.** D. BALAREFF (*Zeitsch. anorg. Chem.*, 1919, 106, 268—280).—In the estimation of phosphoric acid by the double precipitation method, although trustworthy results are obtained, the ignited precipitate is not pure, but contains excess of magnesium and too little phosphoric acid (A., 1918, ii, 406). Neubauer's method for the estimation of magnesium, in which a solution of phosphoric acid is added to the magnesium solution, gives high results when the ammonia is added quickly for the second precipitation, but when the ammonia is added slowly the results approximate to those obtained by Schmitz's method (*loc. cit.*). The use of an alkali phosphate in place of phosphoric acid causes the results to be high on account of the precipitation of alkali magnesium phosphate.

Further experiments on Schmitz's method for phosphoric acid have been made. In this method excess of magnesium chloride is added to the phosphate solution, together with a quantity of ammonium chloride. Sufficient ammonia is then added to the hot solution to cause precipitation as the solution cools. Although this method gives consistent results with widely varying conditions of concentration and proportions of the reacting substances, the conditions for obtaining a pure precipitate of magnesium ammonium phosphate are very circumscribed. More concentrated solutions give purer products, and the purity is increased by diminishing as far as possible the quantity of ammonia used. High results are obtained if too little ammonium chloride is used and the solution is not stirred during the precipitation of the magnesium ammonium phosphate.

With regard to the nature of the impurity accompanying the precipitate, the conditions favouring an impure precipitate are those which would be expected to favour the formation of the compounds  $Mg(NH_4)_2PO_4$  and  $Mg_2(PO_4)_3$ . The former salt, however, should give, on ignition, magnesium metaphosphate, insoluble in hydrochloric acid, but it is found that the precipitate obtained by Schmitz's method is completely soluble, although precipitates formed in the cold contain much metaphosphate (A., 1918, ii, 332). Possibly a second form of metaphosphate exists, soluble in hydrochloric acid, or it may be that other complex compounds are precipitated instead of the above diphosphate. There are grounds for supposing that magnesium ammonium phosphate when ignited undergoes secondary decompositions which have a connexion with the incandescence and blackening which sometimes occur on ignition (compare A., 1917, ii, 90). All experiments on this phenomenon appear to have been made with samples of magnesium ammonium phosphate of doubtful purity, and it is impossible yet to come to any satisfactory conclusions. E. H. R.

**Modified Method of Estimating Arsenic as Ammonium Magnesium Arsenate.** O. BAILLY (*J. Pharm. Chim.*, 1919, [vii], 20, 55—58).—The ammonium magnesium arsenate precipitate, obtained in the usual way, is washed with dilute ammonia, then

with alcohol to remove free ammonia, and titrated with  $N/2$ -acid, using methyl-orange as indicator. Each c.c. of  $N/2$ -acid is equivalent to 0.01875 gram of arsenic.

W. P. S.

**Iodometric Estimation of Arsenic Acid.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 1322—1326).—The reaction  $As_2O_3 + 4HI = As_2O_3 + 2I_2 + 2H_2O$  proceeds from left to right only in strongly acid solution. Accurate titration results are obtained for arsenate concentrations of  $N/5$  to  $N/10$  with a minimum concentration of hydrochloric acid of  $4N$  in the mixture. For more dilute arsenate solutions ( $N/50$ ), a minimum hydrochloric acid concentration of  $4.5N$  is required. After addition of the iodide and the acid to the arsenate solution, five minutes must elapse before titration with thiosulphate.

Molybdate, tungstate, vanadate, manganous, ferrous, uranyl, and chromic ions appear to have no catalytic effect on the reaction.

W. S. M.

**Estimation of Free Alkali or Alkali Carbonate Alone or in the Presence of Alkali Hypochlorite.** W. MESTREZAT (*J. Pharm. Chim.*, 1919, [vii], 20, 9—14. Compare this vol., ii, 79).—Alkali hypochlorite solution, containing no free alkali hydroxide or carbonate, is neutral towards reagents after the hypochlorite has been decomposed by thiosulphate. Free alkali or alkali carbonate in such solution can, therefore, be titrated; alkali carbonates, in the cold and in concentration not exceeding  $N/80$ , are alkaline towards phenolphthalein, but the alkalinity disappears when the titration has proceeded to the formation of alkali hydrogen carbonate.

W. P. S.

**Estimation of Free Alkali Hydroxide and Carbonate in Alkali Hypochlorite Solution.** PHILIBERT (*J. Pharm. Chim.*, 1919, [vii], 20, 52—55. Compare this vol., ii, 79).—A reply to Mestrezat (preceding abstract). The author maintains the trustworthiness of the iodo-acidimetric method.

W. P. S.

**Estimation of Very Small Amounts of Calcium, Magnesium, and Phosphorus in Animal Substances.** L. DIENES (*Biochem. Zeitsch.*, 1919, 95, 131—145).—The methods described are essentially those usually employed, namely, the estimation of calcium as oxalate by titration with permanganate, the estimation of magnesium by the determination of the phosphorus present in the precipitated magnesium ammonium phosphate, and the estimation of phosphorus by titration of the precipitated ammonium phosphomolybdate with standard alkali. The technique of the methods has been suitably modified for the manipulation of very small quantities.

J. C. D.

**Estimation of Zinc and Calcium in the Presence of Lead.** ERNEST NYMAN (*Chem. News*, 1919, 119, 75—76).—Zinc and calcium may be estimated in the presence of lead, in such mixtures as are frequently found in pigments, by the following method. An



acid solution of the salts is treated with ammonia until strongly alkaline and then acidified with acetic acid. Should a precipitate be formed it is dissolved by the addition of a few grams of ammonium acetate. When a clear solution is obtained the solution is made slightly alkaline with ammonia and titrated at 70–80° with standard potassium ferrocyanide solution, using an acid solution of uranyl acetate as external indicator. In this way the zinc may be accurately estimated. To estimate the calcium a faintly alkaline solution is prepared as described above, and the calcium precipitated by the addition of an excess of ammonium oxalate. J. F. S.

#### **Alkalimetric Estimation of Small Amounts of Magnesium.**

P. L. HIBBARD (*J. Ind. Eng. Chem.*, 1919, 11, 753–754).—A method described previously by Bruckmiller (*A.*, 1917, ii, 271) for the titration of ammonium magnesium phosphate is modified by the author in order to render it applicable to the estimation of small amounts of magnesium (5 mg., or less) such as are found in soil extracts. The principal modifications introduced are the use of a Gooch crucible for filtration, whereby the precipitate may be washed with the least possible quantity of solution, washing the precipitate with alcohol and then with a cold saturated ammonium magnesium phosphate solution, and the use of methyl-red as indicator in the titration. W. P. S.

#### **A Colour Reaction which may be Used for the Detection of Mercury in Mercury Compounds.**

ARTHUR ABELMANN (*Pharm. Zentr.-h.*, 1919, 60, 247–248).—The following reaction is given by mercury salts and even by organic mercury compounds in which the mercury does not react with hydrogen sulphide. A solution or suspension of the mercury compound is treated with a drop of dilute nitric acid and a moderate quantity of ferrous sulphate solution, and concentrated sulphuric acid is added so as to form a layer under the mixture; a reddish-violet ring is formed at once at the junction of the two liquids. After some time the usual brown ring (nitric acid reaction) appears above the violet ring. W. P. S.

#### **Volumetric Estimation of Mercury Salts and the Estimation of Mercury in Mercury Chloride Compresses.**

F. UTZ (*Pharm. Zentr.-h.*, 1919, 60, 301–302).—A method described recently by Adanti (*A.*, 1916, ii, 579) was proposed originally by Rupp (*A.*, 1905, ii, 484; 1906, ii, 902), and applied by Utz (*A.*, 1907, ii, 400). W. P. S.

#### **Estimation of Iron in Iron Ores by means of Permanganate.**

L. BRANDT (*Chem. Zeit.*, 1919, 43, 394–397).—The influence of colloidal silica on the titration of ferrous salts with permanganate (compare Schwartz and Rolfes, this vol., ii, 170) in hydrochloric acid solution is not due to its inhibiting action on the reaction between hydrochloric acid and permanganate, since the same effect is noticed in sulphuric acid solutions. The decreased

amount of permanganate required for the titration in the presence of colloidal silica appears to be due to dissolved and atmospheric oxygen, the silica acting as a catalyst in the oxygen-ferrous salt-permanganate reaction. Silica has no influence on the reaction between oxygen and ferrous salts in the absence of permanganate.

W. P. S.

**Analysis of Steel.** A. TRAVERS (*Ann. Chim.*, 1919, [ix], 11, 17—128. Compare this vol., ii, 81, 300).—An exhaustive résumé of methods for the estimation of the usual constituents of steels; the original should be consulted for the many methods which are given in detail. [See, further, *J. Soc. Chem. Ind.*, 724A.]

W. P. S.

**Estimation of Iron, Zinc, Copper, and Aluminium in Aluminium Alloys.** PAUL HOLMSEN (*Tidskr. Kemi. Farm. Ter.*, 1919, 16, 62—63).—The separation of copper, iron, aluminium, and zinc is effected by treating the sample with 30% sodium hydroxide solution, using 50 c.c. for a 3-gram sample. When the aluminium and zinc are in solution, water is added, and the residue of iron and copper removed by filtration. Aluminium is separated from zinc and iron from copper by adding ammonia to the acid solutions of these two pairs, and the four metals are estimated by well-known methods.

CHEMICAL ABSTRACTS.

**Electrolytic Estimation of Nickel and Cobalt.** MOTOOKI MATSUI and TADASU NAKAZAWA (*J. Tokyo Chem. Soc.*, 1919, 40, 339—349).—Nickel and cobalt can be precipitated quantitatively from their dimethylglyoxime salts by electrolysis. The following modification is therefore substituted for the usual method. To the mixture of nickel and cobalt, sodium acetate and an excess of dimethylglyoxime (0.2 gram) are added until the precipitation of nickel is complete. The precipitate is washed, dissolved in sodium hydroxide (4.8 grams), and estimated by electrolysis. To the filtrate is added sodium hydroxide, and the cobalt estimated similarly. When the amount of nickel exceeds 0.058 gram in 100 c.c., an addition at the positive pole of a few drops of a mixture containing 5 c.c. of glycerol, 45 c.c. of alcohol, and 50 c.c. of water is necessary in order to prevent deposition of the oxide at the pole. When cobalt is present in a high concentration, the similar oxide deposit can be prevented if aqueous ammonia (50 c.c.) containing 2 grams of ammonium sulphate, to increase the conductivity, is substituted for sodium hydroxide. From a mixture containing 0.0102 gram of nickel and 0.1836 gram of cobalt made up to 100 c.c., using 3.2 volts for nickel, 3.8 volts for cobalt, with one ampere current, were obtained 0.0100 gram of nickel after 2.5 hours and 0.1834 gram of cobalt after 3.3 hours at the ordinary temperature. The temperature should always be kept under 50°, otherwise the positive pole will be coated with the oxide.

CHEMICAL ABSTRACTS.

**Analysis of Alloys of Tin.** ARCHIBALD CRAIG (*J. Ind. Eng. Chem.*, 1919, 11, 750—753).—A discussion of the conditions giving the most trustworthy results in the analysis of tin alloys by the nitric acid separation method; the processes for the various separations and purification of the precipitates, etc., are given in detail. W. P. S.

**Separation of Tin, Antimony, and Arsenic by Plato's Method.** WILLY HARTMANN (*Zeitsch. anal. Chem.*, 1919, 58, 148—156).—Modifications of this method (A., 1910, ii, 903) are described. After antimony and arsenic have been distilled, as in the original method, the residue is treated with a mixture of hydrobromic and hydrochloric acids, and the tin distilled at 130° to 140° in a current of carbon dioxide. Arsenic is separated by treating the distillate, in the cold, with hydrogen sulphide; the arsenic trisulphide is collected on a filter, and the antimony is also precipitated as sulphide after the filtrate has been neutralised with ammonia. W. P. S.

**Estimation of Cerium in the Presence of other Rare Earths by Precipitation as Ceric Iodate.** PAUL H. M.-P. BRINTON and C. JAMES (*J. Amer. Chem. Soc.*, 1919, 41, 1080—1085).—Solutions containing rare earth nitrates (thorium having been removed) may be quantitatively analysed for cerium as follows: the solution is treated with half its volume of nitric acid; the whole solution at this stage should not be more than 75 c.c., and the amount of cerium oxide should not exceed 0.15 gram; 0.5 gram of potassium bromate is added, and when it has dissolved ten to fifteen times the theoretical quantity of potassium iodate is added in nitric acid solution (100 grams iodate, 333 grams acid) with constant stirring. The ceric iodate is allowed to settle and filtered on a paper of close texture. After draining, the precipitate is washed back into the beaker by means of a solution containing 8 grams of potassium iodate and 50 c.c. of nitric acid per litre. The precipitate is well mixed with the washing solution and brought back on to the same filter paper. It is then rinsed back into the beaker with hot water, heated to boiling, and treated drop by drop with nitric acid until it is entirely dissolved. To this solution, 0.25 gram of potassium bromate and as much iodate as was previously used are added. The precipitate is allowed to settle and then filtered through the same filter paper, and washed once with the washing solution. It is brought back into the beaker, well stirred, and again filtered and washed with three small portions of the washing solution. The filter paper and precipitate are now dropped into the original beaker, and 5—8 grams of oxalic acid and 50 c.c. of water are added. The beaker is covered and gently heated, and then boiled until iodine is no longer expelled. The precipitate is kept several hours,

filtered, washed, dried, and ignited to oxide, which is weighed. This method is trustworthy even in the presence of large quantities of the other rare earths.

J. F. S.

**Electrometric Titration of Vanadium. Selective Oxidation of Vanadyl Salts in Presence of Chromic Salts.** G. L. KELLEY, J. A. WILEY, R. T. BOHN, and W. C. WRIGHT (*J. Ind. Eng. Chem.*, 1919, 11, 632—634).—For the estimation of small quantities of vanadium in steel by the method of electrometric titration (A., 1917, ii, 512), the sample is dissolved in sulphuric acid and the vanadium oxidised by boiling with nitric acid under specified conditions. This oxidises vanadyl compounds to the extent of about 99% without oxidising chromic compounds. The liquid is then cooled and titrated by the electrometric method with ferrous ammonium sulphate which has been standardised against potassium dichromate solution. A correction is subsequently made for the 1% of unoxidised vanadium. In estimating chromium in chrome-vanadium steels, the solution, obtained as described, is oxidised with nitric acid, and then treated with silver nitrate solution and ammonium persulphate solution, boiled to decompose the excess of persulphate, acidified with hydrochloric acid, boiled and cooled, and the chromium and vanadium titrated together. The vanadium end-point is that previously described (*loc. cit.*). The result for vanadium is expressed in its equivalent of chromium and deducted from the total dichromate solution used in the titration of the chromium and vanadium. [See also *J. Soc. Chem. Ind.*, 1919, 583A.]

C. A. M.

**Microchemical Reaction of Various Bismuth Compounds.**

G. DENIGÈS (*Bull. Soc. pharm. Bordeaux*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 213—214).—A drop of dilute hydrochloric acid and a drop of 5% hexamethylenetetramine solution are mixed on a microscope slide, and a drop of a bismuth solution or a small particle of an insoluble bismuth compound is brought into contact with the mixture. On examining the preparation under the microscope (a cover-glass is not used), characteristic crystals are observed, mainly at the point of contact. The crystals are colourless and have the form of hexahedra, hexagonal plates, dodecahedra, or rhombic octahedra. The crystals may be obtained from practically all bismuth compounds.

W. P. S.

**Electroanalysis of Bismuth and its Ores.** MANZO NAKAO

(*J. Pharm. Soc. Japan*, 1919, No. 446, 275—307).—The formation of spongy and loose granular precipitates at the negative pole is one of the sources of error and difficulties in the electroanalysis of bismuth. Sand's method, although it prevents the formation of the spongy deposit, does not produce sufficiently permanent precipitates that will not easily peel off on drying. The

author modifies the methods used by Sand and Fischer by proposing the use of a very small amount of colloidal substances. An addition of 1 mg. of gum arabic to 100 c.c. of the solution not only produces a more permanent precipitate of bismuth, but also gives a quantitative yield in ten minutes. In separating bismuth from copper, the formaldehyde used by Sand to prevent the formation of bismuth oxide is replaced by borax and hydroxylamine sulphate. The best result is obtained by using sodium tartrate 4 grams, sodium hydroxide 4 grams, potassium cyanate 3.5 grams, hydroxylamine 0.5—1 gram, borax 2—1 grams, made up to 120 c.c., stirring at the rate of 1200 revolutions per minute at 65° for twenty minutes, employing 0.4—0.2 ampere, and maintaining 1.2—1.7 volts at the poles. Under this condition, 0.3131 gram out of 0.3130 of bismuth is obtained in the separation from 0.3 gram of copper. In estimating bismuth in bismuth ores, after removing tin and lead, instead of using hydrogen sulphide, ammonia and ammonium chloride are employed, the mass is dissolved in as little nitric acid as possible, and 4 grams of tartrate, 2 grams of sodium hydroxide, 5 grams of potassium cyanate, and 1 gram of hydroxylamine are added, the volume being made up to 120 c.c., and a current of 1.2 volts used. When the voltage exceeds 1.2, the current is changed to 0.1 ampere; above 1.8 volts, 2 amperes, and finally 0.5 ampere, of current are used for thirty-five minutes (70—80°), stirring at the rate of 1000 revolutions per minute.

CHEMICAL ABSTRACTS.

**Estimation of the Inorganic Constituents of Blood and other Physiological Material.** ISIDOR GREENWALD (*J. Biol. Chem.*, 1919, **38**, 439—440).—Proteins and fats are removed from the blood by precipitation with picric acid. The oxidation of the filtrate for the purpose of estimating the inorganic constituents is then an easy matter.

J. C. D.

**Use of the Critical Temperature of Solution in Aniline in the Summary Analysis of a Petroleum.** G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **169**, 70—73).—By summary analysis, the authors mean a determination of the percentage of aromatic hydrocarbons (*Ar*), saturated cyclic hydrocarbons (*C*), and acyclic hydrocarbons (*Ac*) present in the petroleum. The critical temperatures of solution of the petroleum in aniline are determined before and after its treatment with a mixture of sulphuric and nitric acids to remove the aromatic hydrocarbons, the two values obtained being respectively  $T_1$  and  $T_2$ . Then the respective percentages may be calculated from the three formulæ  $Ar = 1.18(T_2 - T_1)$ ,  $C = [72 - (T_2 + 0.2)](100 - Ar)/(72 - 39.5)$ , and  $Ac = 100 - Ar - C$ . These formulæ contain all necessary corrections except for the presence of ethylenic hydrocarbons. If these are present, for  $T_1$  must be written  $T_1 + 0.4E$ , where  $E$  is the percentage of ethylenic hydrocarbons expressed as amylene.

W. G.

**Critical Temperatures of Solution in Aniline of Mixtures of Hydrocarbons. Application to the Analysis of Petroleum.**

J. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, 169, 85—188. Compare preceding abstract).—A mixture of two acyclic hydrocarbons or a mixture of one acyclic and one saturated cyclic hydrocarbon obeys the law of additivity in so far as its critical temperature of solution in aniline is concerned, but a mixture of two saturated cyclic hydrocarbons does not obey this law. If to a mixture of hydrocarbons, devoid of aromatic hydrocarbons, benzene is added to an extent not exceeding 10—15%, then the depression of the critical temperature of solution in aniline is proportional to the percentage of benzene added, the ratio being 1:1.14. Similarly, for toluene the ratio is 1:1.19 and for xylene 1:1.24. The above results furnish the basis for the method of analysis of petroleum previously outlined (preceding abstract), it being necessary first to fractionate the petroleum so that there is only one saturated cyclic hydrocarbon in each fraction. W. G.

**The Composition of some Asiatic Petroleums.**

G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, 169, 285—288).—Using the analytical method based on the critical temperature of solution in aniline, previously described (this vol., ii, 267; preceding abstracts), the authors have determined the composition of petroleums coming from Persia, Sumatra, and Borneo. The Persian and Sumatran petroleums are particularly rich in acyclic hydrocarbons. The Borneo petroleum was fractionated, and the different fractions were examined separately. Further details are given for the correction necessary in the calculation due to the presence of ethylenic hydrocarbons. W. G.

**Estimation of Thiophen.** PERCY E. SPIELMANN and S. P.

SCHOTZ (*J. Soc. Chem. Ind.*, 1919, 38, 188—189r).—A modified basic mercuric sulphate method is recommended for the estimation of thiophen in benzene. Two c.c. of the sample are shaken for three hours in a closed tube with 20 c.c. of basic mercuric sulphate solution (sulphuric acid, 20 c.c.; mercuric oxide, 5 grams; water, 100 c.c.). The precipitate formed is collected, washed with hot water, dried at 110°, and weighed; its weight multiplied by 0.0757 gives the amount of thiophen in 2 c.c. of benzene. Another, but less convenient, method consists in heating 10 c.c. of the benzene at 100° for fifteen minutes with 4 grams of basic mercuric acetate (glacial acetic acid, two parts; mercuric oxide, one part). After cooling, the precipitate is collected, washed with water, dried at 110°, and weighed. In this case, the factor is 0.07516. W. P. S.

**Use of Refraction in Analysis.** O. FAUST (*Zeitsch. anal. Chem.*, 1919, 58, 145—148).—The refractometer may be used for estimating alcohol in mixtures of alcohol and water, provided that the amount of alcohol lies between 0 and 40%. The maximum refraction is given by alcohol of about 80%, and decreases as the

concentration rises or falls, so that between 50 and 100% there are always two mixtures having the same refraction. W. P. S.

**Estimation of Ethyl Alcohol in the Presence of Volatile Substances, especially Aldehyde and Acetone, and the Simultaneous Estimation of the Latter.** KARL HOEPNER (*Zeitsch. Nahr. Genussm.*, 1917, **34**, 453—466).—The following procedure is recommended for the estimation of ethyl alcohol, acetaldehyde, and acetone in a mixture of the same in aqueous solution. Ethyl alcohol and acetaldehyde are oxidised to acetic acid by means of chromic acid and sulphuric acid; the unchanged acetone is then distilled and converted into the ketoxime by treatment with hydroxylamine hydrochloride; an equivalent quantity of hydrochloric acid is liberated in the reaction, and its titration gives the amount of acetone present. Acetaldehyde and acetone are then converted into the aldoxime and ketoxime by similarly treating a quantity of the original solution with hydroxylamine hydrochloride; the difference between the quantity of hydrochloric acid liberated in this and in the previous experiment is a measure of the aldehyde present. Ethyl alcohol and acetaldehyde are then estimated together by oxidation with chromic acid. [See, further; *J. Soc. Chem. Ind.*, 1919, 735A.] W. P. S.

**Titration of Sugars.** E. RUPP and F. LEHMANN (*Zeitsch. Nahr. Genussm.*, 1919, **37**, 162—164).—Further experience confirms the trustworthiness of the method described previously by the authors (*A.*, 1909, ii, 442). If desired, the sugar solution may be mixed with the cold Fehling's solution and water, and the mixture then boiled, etc., as described. (Compare also Frerichs and Mannheim, *A.*, 1917, ii, 393.) W. P. S.

**Influence of Acetone on Bang's Method of 1914 for the Estimation of Sugar.** N. O. ENGFELDT (*Svensk Farm. Tidskr.*, 1919, **23**, 301—308).—The statement has been made by G. Engstrand that acetone reacts with the iodine in the Bang method for the estimation of sugar in blood and urine, causing an error in the results. The author has made several careful tests, using blood, acetone, and  $\beta$ -hydroxybutyric acid. The titrations were not affected by these two substances, and the results in using this method are trustworthy. CHEMICAL ABSTRACTS.

**Estimation of Sugar in Blood.** HUGH MACLEAN (*Biochem. J.*, 1919, **13**, 135—147).—Improvements and simplification of the method previously published by the author (*A.*, 1916, i, 613) are described. The greater part of the protein is removed by heating with an acetic acid-sodium sulphate solution, the remainder being removed by a small quantity of dialysed iron. The sugar in an aliquot portion of the protein-free filtrate is estimated by boiling with an alkaline copper solution containing potassium iodide and iodate. Careful regulation of the boiling is necessary to ensure accurate results. The solution containing the cuprous oxide in

suspension is cooled, treated with a slight excess of hydrochloric acid, and the free iodine titrated with sodium thiosulphate. The method yields accurate results with as little as 0.2 c.c. of blood.

J. C. D.

**The Picric Acid Method for the Estimation of Sugar in Blood, and a Comparison of this Method with that of Maclean.** OWEN LAMBERT VAUGHAN DE WESSELOW (*Biochem. J.*, 1919, **13**, 148—152).—A study of the two methods indicated that the results yielded by Benedict's method were invariably higher than those obtained by Maclean's method (see preceding abstract). The possible causes of the discrepancy were considered, and it was found that the high figures given by the first-named method appear to be chiefly due to the presence of an interfering substance or substances, mainly concentrated in the corpuscles, which reacts with the picric acid solution at an early stage of the heating. The Maclean method is therefore considered to be the more accurate one of the two.

J. C. D.

**Lewis-Benedict Method of Estimating Blood Sugar.** SERGIUS MORCULIS and H. M. JAHR (*J. Biol. Chem.*, 1919, **39**, 119—123).—The presence of creatinine increases the blood sugar value as determined by the Lewis-Benedict method, particularly in the analysis of pathological bloods when the blood creatinine may be high (compare de Wesselow, preceding abstract).

J. C. D.

**The Cuprous Chloride-Iodine Method for Reducing Sugars Simplified.** F. M. SCALES (*J. Ind. Eng. Chem.*, 1919, **11**, 747—750. Compare A., 1916, ii, 117; 1917, ii, 276).—Twenty c.c. of modified Benedict's solution (copper sulphate, 16.0 grams; sodium citrate, 150 grams; anhydrous sodium carbonate, 130 grams; sodium hydrogen carbonate, 10 grams per litre) and 10 c.c. of the sugar solution (containing not more than 0.02 gram of dextrose) are mixed, heated gradually so as to boil in five minutes, boiled for a further three minutes, and cooled rapidly. The solution is acidified with 100 c.c. of dilute acetic acid, an excess of iodine solution is added, followed by 25 c.c. of dilute hydrochloric acid, and the excess of iodine is titrated with thiosulphate solution after the lapse of one minute. The thiosulphate solution may be standardised against known amounts of dextrose: the ratio of reducing sugar to thiosulphate is constant.

W. P. S.

**Studies in Steam Distillation. The Possibilities and Limitations of Duclaux's Method for the Estimation of Homologous Acids.** H. DROOP RICHMOND (*Analyst*, 1919, **44**, 255—274. Compare A., 1917, i, 316).—A series of tables is given recording the author's experimental results and showing the quantity of each acid distilled for each 10% by volume distilled, the tables being divided according to the initial strength of acid. Methods of calculation are discussed, and the application of



Duclaux's method in analysis is described; attention is drawn to its usefulness in estimating volatile acids, the purity of an acid, the quantity of impurity present, etc.

W. P. S.

**Estimation of  $\beta$ -Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Blood.** DONALD D. VAN SLYKE and REGINALD FITZ (*J. Biol. Chem.*, 1919, **39**, 23).—In the process previously described by these authors (A., 1918, ii, 86) it is necessary that the precipitate should be filtered soon after the period of boiling is ended.

J. C. D.

**Detection of Formaldehyde and Hexamethylene-tetramine in Urine.** F. URZ (*Süddent. Apoth. Zeit.*, 59, 55—56, 64; from *Chem. Zentr.*, 1919, ii, 820—821).—The author's investigations show that the time within which formaldehyde can be detected in the urine after administration of hexamethylene-tetramine varies in an extraordinary degree; generally an hour elapses before the detection is successful. The most suitable methods are those of Lebbin, Salkowski, Jorissen and Judd, Collins and Hanzlik, and, particularly, the phenylhydrazine test described by Arnold and Mentzel. When the amount of formaldehyde is very small or the urine is deeply coloured, the specimen is conveniently treated with phenylhydrazine and potassium ferricyanide and shaken with ether; the ethereal solution is agitated with concentrated hydrochloric acid. The red coloration thereby produced appears in the acid layer after the two liquids have separated.

The main portion of hexamethylenetetramine separates as such in the urine. Mercuric chloride in the presence of 10% of alcohol is a suitable precipitant for hexamethylenetetramine, the mode of operation recommended by Schröter being particularly suitable. Precipitation by bromine water gives a useful qualitative test for the presence of hexamethylenetetramine in urine. Esbach's method cannot be applied to the estimation of albumin in urines which contain hexamethylenetetramine; care is also necessary in testing such urines for sugar.

H. W.

**Titration of *p*-Aminoazobenzene.** F. NEITZEL (*Chem. Zeit.*, 1919, **43**, 472).—Trustworthy results may be obtained by diazotising the substance in acid-alcoholic solution. One gram of the sample is dissolved in 100 c.c. of alcohol and 5 c.c. of hydrochloric acid, D 1.19, and the solution is titrated with standardised nitrite solution; iodide-starch paper is used as an external indicator.

W. P. S.

**Applicability of Cuprammonium Sulphate for the Acidimetric Estimation of Alkaloids according to E. Falières.** HERMANN KUNZ-KRAUSE and RUDOLF RICHTER (*Arch. Pharm.*, 1917, **255**, 507—513).—The method suggested by Falières (A., 1899, ii, 713) for the acidimetric estimation of alkaloids in their pure solutions by means of standard cuprammonium solution yields satisfactory results, although the high value of the ratio between corresponding volumes of *N*/10-sulphuric acid and the cuprammon-

um solution detracts from its sensitiveness; the latter is indeed far below the sensitiveness of the iodeosin method, which admits of the use of  $N/100$ -solutions. The Falières method cannot be applied to the estimation of alkaloids in tinctures, extracts, etc., preliminary separation of the alkaloids being necessary if it is to be employed. See *J. Soc. Chem. Ind.*, 1919, 737A.]

T. H. P.

**Estimation of Caffeine in Vegetable Material.** FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1919, **41**, 1298—1306).—The process for estimating caffeine in tea, described in Allen's "Commercial Organic Analysis," has been considerably modified so as to make it suitable for the analysis of vegetable material generally. The new method is as follows. Ten grams of the finely ground material are extracted for about eight hours with hot alcohol, the extract is added to a suspension of 10 grams of heavy magnesium oxide in 100 c.c. of water, and the whole slowly evaporated nearly to dryness, with frequent stirring. The powder is transferred to a smooth filter and washed with hot water until about 250 c.c. of filtrate collects, when the solution is mixed with 10—20 c.c. of 10% sulphuric acid, and then boiled in a litre flask for about thirty minutes, in order to hydrolyse saponins. The cooled liquid is filtered through a moistened paper into a separating funnel, and shaken with six portions of chloroform of 25 c.c. each. The extracts are decolorised by shaking with 5 c.c. of 1% potassium hydroxide, then run through a dry filter into a conical flask and evaporated, and the caffeine is transferred to a tared beaker and dried in a water-oven. Generally speaking, the residue is nearly white.

Some examples of the application of the method to teas, coffee, coffee leaves and pulp, and guarana are recorded. It is also stated that the "Forest tea" of the Philippines, *Ehretia macrophylla*, Wall, the "New Jersey tea," *Ceanothus Americanus*, Linn., and the "wild coffee" of Florida, *Psychotria undata*, Jacq., do not contain caffeine.

J. C. W.

**Estimation of Morphine and Solubility of Morphine in Ammonia.** A. HEIDUSCHKA and M. FAUL (*Arch. Pharm.*, 1917, **255**, 441—466).—The solubility of morphine in ammonia solutions is found to be proportional to the concentration of the hydroxyl ions of the solution. From the solubility results, a formula is elaborated for correcting the values given by the method of estimating morphine in opium based on the precipitation of the base by ammonia. [See *J. Soc. Chem. Ind.*, 1919, 737A.]

T. H. P.

**Estimation of Quinine in Urine.** BAUR and REVELLET (*Union pharm.*, 1918; from *Ann. Chim. anal.*, 1919, [ii], **1**, 214—215).—Five c.c. of the filtered urine containing quinine are mixed with 5 c.c. of picric acid solution, and the turbidity obtained is compared with that produced by known amounts of quinine added to normal urine and treated similarly. The method cannot

be applied to urines containing albumin, large quantities of potassium or ammonium salts, or urates. W. P. S.

**Specific Colour Reaction of Oxalates.** H. CARON and D. RAQUET (*Ann. Chim. anal.*, 1919, [ii], 1, 205).—A reaction described previously (this vol., ii, 351) for the detection of manganese may be used inversely for the detection of oxalates. A red coloration is obtained when an oxalate solution is treated with two drops of 10% manganese sulphate solution, 1 c.c. of acetic acid, and one drop of potassium dichromate solution or a few drops of alkali hypochlorite solution. In the case of an acid solution or of oxalic acid itself, the acetic acid used in the test should be replaced by sodium acetate. The coloration may be obtained with 0.1 gram of oxalic acid; phosphoric acid and hydrofluoric acid do not interfere with the test. W. P. S.

**Glucosides with Digitalis-like Action. A New Characteristic Reaction.** H. BALJET (*Pharm. Weekblad*, 1918, 55, 457—467).—Digitalin gives a deep red coloration with picric acid and potassium or sodium hydroxide. Gitalin, digitoxin, anhydrogitalin, strophanthin, and *K*-strophanthin give an orange-red coloration with the same reagents. All these glucosides exert an action similar to that of digitalis on the heart. Digitonin, arbutin, amygdalin, and conduragin do not respond to the test. The author suggests that the effect is due to the presence of the carbonyl group linked directly to a carbon atom, such as occurs in the lactone structure of the digitalis glucosides. A positive reaction is also obtained with peptones, probably owing to the presence of creatinine, with acetone, and with aldoses. W. S. M.

**A Revised Colorimetric Method for the Estimation of Uric Acid in Urine.** OTTO FOLIN and HSIEN WU (*J. Biol. Chem.*, 1919, 38, 459—460).—The method previously described for the estimation of uric acid in blood (Folin and Wu, this vol., ii, 308) may be employed in the analysis of urine. J. C. D.

**A Colour Reaction of the Proteins.** S. EDLHACHER (*Zeitsch. physiol. Chem.*, 1919, 105, 240—241).—The protein solution is shaken with a solution of sodium hydroxide and methyl sulphate, and, after the decomposition of the latter, concentrated sulphuric acid is added so as to form a layer at the bottom. At the surface of contact of the two layers a reddish-blue colour develops, and, on shaking, the whole liquid assumes this colour.

The coloration resembles that produced in the glyoxylic acid reaction, and, as in that test, is produced by tryptophan. Indole and scatole give a red coloration. The test is regarded as more sensitive than the bromine reaction for free tryptophan.

J. C. D.

**The Starch-Iodine Reaction and its Application in the Colorimetric Estimation of Proteins in Immunity Reactions.** C. LANGE (*Biochem. Zeitsch.*, 1919, 95, 46—84).—A very full discussion of the reaction of starch with iodine, including a

criticism of Wohlgemuth's method for estimating diastase. The reaction between starch and iodine may be influenced by the presence of other substances, particularly protein, and this fact is made the basis of a method for estimating protein in such fluids as blood, plasma, serum, or bacterial vaccines. The fluids to be compared are treated with a solution of iodine, and, after suitable dilution, are heated for half an hour on the water-bath at 40°. Starch is then added and the colours compared. This process may be used for the standardisation of vaccines.

J. C. D.

**Application of Pyramidone in Analysis.** ESCAICH (*J. Pharm. Chim.*, 1919, [vii], 20, 49—52).—Pyramidone in acid solution gives a blue coloration with many oxidising substances (nitrites, ferric chloride, hydrogen peroxide, etc.), but if pyridine is added, a sensitive reagent is obtained for the detection of anaerobes in blood, raw milk, etc. A blue coloration develops when 1 c.c. of urine containing blood is added to a mixture of 1 c.c. of pyridine, 1 c.c. of pyramidone solution, two drops of hydrogen peroxide, and a few drops of acetic acid. A mixture of pyramidone, dilute copper sulphate solution, and acetic acid gives a blue coloration and a turbidity when treated with a few drops of hydrocyanic acid solution; inversely, this reaction may be used for the detection of copper.

W. P. S.

**Methods of Blood Analysis. I. Critical Review of the Methods for Removing Proteins.** M. RICHTER-QUITNER (*Biochem. Zeitsch.*, 1919, 95, 179—204).—The importance of this phase of blood analysis is emphasised. Removal of proteins by means of precipitation with salts of heavy metals results in low values being obtained for non-protein nitrogen in the filtrate, because the precipitate adsorbs substances such as urea and creatinine. The same drawback applies to the use of colloidal precipitants such as dialysed iron. The removal of proteins by heat is very difficult to carry out satisfactorily.

Of the acid precipitants, the author gives the preference to tri-bromoacetic acid, but, as in the case of heat precipitation, the values for non-protein nitrogen tend to be high.

A modification of Folin's method for removing protein by methyl alcohol and zinc chlorides is described which gives trustworthy results.

J. C. D.

**Precipitation of Proteins by Ammonium Sulphate and Biochemical Reactions.** A. CH. HOLLAENDER (*Compt. rend. Soc. Biol.*, 1919, 567; from *J. Pharm. Chim.*, 1919, [vii], 20, 92—94).—Preliminary precipitation of proteins by ammonium sulphate is recommended before precipitin reactions are applied. For instance, urine containing ovalbumin is saturated with ammonium sulphate, the precipitate collected, washed with saturated ammonium sulphate solution, then dissolved in sodium chloride solution, and the albumin identified by precipitin reactions.

W. P. S.

**Identification of Pharmaceutical Disulphones, Sulphonal, Trional, and Tetronal.** J. A. SANCHEZ (*El Restaurador farm.*, 1918; from *Ann. Chim. anal.*, 1919, [ii], 1, 228—229).—The three substances yield iodoform when treated as follows: A mixture of equal quantities of the sulphone and manganese dioxide is heated in a test-tube, and the vapours evolved are collected in a small quantity of water contained in a second test-tube; the solution thus obtained has an odour of ethyl mercaptan, and when rendered alkaline with sodium hydroxide, heated, and treated with iodine solution, yields iodoform. The three substances may be distinguished from one another by the melting points and by their different solubilities in ether. One gram of sulphonal dissolves in 133 c.c. of ether, 1 gram of trional in 15.57 c.c., and 1 gram of tetronal in 9.83 c.c. W. P. S.

**Identification and Assay of Pharmaceutical Disulphones.** SCHAMELHOUT (*J. Pharm. Belg.*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 259—260).—Several errors in a recent paper by Sanchez (preceding abstract) are pointed out; sulphonal, trional, and tetronal do not contain a CO group, the ethylsulphonic group does not contain a CH<sub>3</sub> group, and the iodoform reaction is not characteristic of ethylsulphonic groups. W. P. S.

**Silver Sodium Salvarsan.** I. A. BINZ (*Arbb. aus. Inst. exp. Therapie Georg. Speyer Hause*, 1919, 7, 43—47; from *Chem. Zentr.*, 1919, iv, 37).—Silver is deposited as silver oxide when silver sodium salvarsan is oxidised by hydrogen peroxide in alkaline solution, and the arsenic is converted into a state in which it can readily be detached from the nucleus in the form of arsenic acid, the latter process being advantageously effected with sodium hypochlorite. The method of removing arsenic from organic compounds is not universally applicable in its present form; arsenobenzene gave low results. The analysis of silver sodium salvarsan is performed as follows: The substance (0.6232 gram) is heated to boiling for an hour with water (30 c.c.) and perhydrol (6 c.c.); after addition of concentrated nitric acid (9 c.c.), the solution is evaporated to dryness, when the silver (except for a trace of silver chloride due to the presence of sodium chloride in the preparation) is converted into silver nitrate. The residue is boiled under a reflux condenser for an hour with a solution of sodium hypochlorite (30 c.c.), whereby the silver is completely converted into silver chloride and the arsenic is eliminated. [The hypochlorite solution is prepared by dropping a mixture of water (11 c.c.) and hydrochloric acid (D 1.19; 84 c.c.) on potassium permanganate (13 grams), and absorption of the chlorine in sodium hydroxide solution (10*N*; 60 c.c.) and water (150 c.c.)]. Arsenic is estimated in the filtrate by means of magnesia mixture after decomposition of the excess of hypochlorite with boiling hydrochloric acid, dilution with water, and filtration of silver chloride. H. W.

